Contribution from the Department of Chemistry
University of Florida, Gainesville, Florida 32601, U.S.A.

The Crystal Structure of Catena-μ-bis-(1,2-diphenylphosphinyl)ethane-Dichlorocopper(II)

M. Mathew and G.J. Palenik[1]

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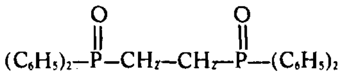
The crystal structure of the compound with stoichiometry $CuCl_2$. bis(1,2-diphenylphosphinyl)ethane has been determined from three dimensional X-ray diffraction data collected on a General Electric XRD-6 automatic diffractometer, using Cu–Kα radiation and the stationary crystal-stationary counter technique. The monoclinic cell for the greenish-blue crystals has dimensions of $a = 12.206(2)$, $b = 20.172(4)$, $c = 10.559(1)$ Å and $\beta = 97.26(2)$ Å. The space group is C2/c and, with 4 molecules per unit cell, D_c is 1.454 g/cm^3 and D_m is 1.46 g/cm^3. The structure was determined by the heavy atom method and refined by full matrix least-squares techniques to a final R of 0.047 for the 2161 observed reflections used in the analysis. The Cu atom lies on a 2-fold axis and the bis(1,2-diphenylphosphinyl) ethane ligand lies on a center of symmetry. The crystal consists of infinite chains of $CuCl_2$ units linked by the phosphine oxide which is functioning as a bridging rather than chelating ligand. A comparison of the Cu–O distance of 1.959(3) Å with the value in other oxo-adducts reveals a remarkable consistency of Cu–O bonds lengths, while the Cu–Cl distances (2.195(1) Å in the present complex) vary depending on the nature of the oxo-molecule. The fact the Cu–O distance is independent of the nature of the oxo donor molecule but that the Cu–Cl distances vary has not been noted previously.

Introduction

Structural studies of various pyridine-N-oxide complexes of copper(II) halides have revealed a variety of configurations, many of which contain bridging N-oxide molecules.[2-6] In contrast to the vast numbers of N-oxide complexes that have been studied, only a meager amount of structural data for other oxo-species are available.[7-8] Therefore, when a number of phosphine oxide complexes of Cu^{II} compounds were prepared by the reaction of a phosphine with the Cu^{II} salt,[9] we decided to investigate the resulting oxo-adducts.

The reaction of bis(1,2-diphenylphosphine)ethane, with copper(II) chloride yields a product which is rapidly oxidized in air to the compound dichlorobis-(1,2-diphenylphosphinyl)ethane copper(II). The ligand (I) will be henceforth abbreviated as DPPO.



$$(C_6H_5)_2\overset{\overset{O}{\|}}{P}-CH_2-CH_2-\overset{\overset{O}{\|}}{P}-(C_6H_5)_2$$

The compound can also be prepared by the reaction of DPPO with copper(II) chloride.[10] If the DPPO ligand functions as a bidentate chelate, the $CuCl_2$. DPPO complex would contain a relatively rare seven-membered chelate ring system. A crystal structure study of the $CuCl_2 \cdot$ DPPO complex was undertaken to investigate the possibility of a seven-membered chelate ring and to provide data on an oxo-adduct of copper(II) chloride. A preliminary report of our results showed that the DPPO ligand is bridging and not chelating, with the Cu^{II} atom in the center of a distorted tetrahedron.[11]

Experimental Section

Recrystallization of the compound $CuCl_2 \cdot$ DDPO from *n*-butanol gave greenish-blue crystals. Preliminary precession and Weissenberg photographs indicated monoclinic symmetry. The systematic absences of $hk\ell$ for $h+k = 2n+1$ and $h0\ell$ for $\ell = 2n+1$ indicated that the probable space groups were Cc (C_s^4) or C2/c (C_{2h}^6). An analysis of the intensity distribution by the standard method of Howells, Phillips, and Rogers indicated that C2/c was the most probable space group.

A small equidimensional crystal (0.15 mm along an edge) was used for the intensity measurements. The unit cell dimensions were determined by a least-squares fit of 20 two-theta values (in the range of 30 to 50°) measured for the Cu–K$_\beta$ ($\lambda = 1.39217$ Å) peak. The final values, together with their estimated standard deviations, are $a = 12.206(2)$, $b = 20.172$ (4), $c = 10.559(1)$ Å and $\beta = 97.26(2)°$. The density calculated for 4 molecules of $CuCl_2C_{26}H_{24}P_2O_2$, M.W. of 564.86, is 1.454 g/cm^3, in good agreement

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[1] Research performed at the Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.

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with the value of 1.46 g/cm^3 measured by flotation.

The intensity data were collected using a General Electric XRD-6 automatic diffractometer employing the stationary crystal-stationary counter technique. The radiation used was CuK$_{\alpha1}$ (λ = 1.54051 Å) with reasonable monochromatization achieved by means of a nickel filter and pulse height analyzer. All the reflections in the unique set for which $2\theta < 135°$ (for CuK$_{\alpha1}$) were measured first and then the entire hemisphere with $2\theta < 135°$ was remeasured. A total of 7688 intensity measurements was made, with up to three measurements being recorded for the major portion of the unique set. A small correction (maximum 3%) was applied for the variation of 4 standard reflections which were measured after every 100 reflections. The reflections which are equivalent because of symmetry were averaged to give 2339 independent reflections. A background curve as a function of 2θ was derived from a measurement of the background at various points in reciprocal space free from streaking or reflections. The 2161 reflections that were greater than 1.2 times the background count were considered to be observed and used in the analysis. The remaining 178 reflections were given a value of 0.1 times the background and were considered as unobserved. An empirical correction for the α_1—α_2 splitting was made; these data were then reduced to a set of amplitudes on an arbitrary scale by the application of Lorentz-polarization corrections. No absorption corrections were made because the value of μ was 44.6 cm^{-1}, but μr was only 0.3.

Structure Determination and Refinement. The positions of the Cu, Cl, and P atoms were determined from a sharpened three-dimensional Patterson function. The space group was assummed to be C2/c from the intensity statistics and the Patterson was interpreted on this basis. A Fourier synthesis was computed, with the phases determined by the three heavy atoms; the positions of all the remaining non-hydrogen atoms were found easily. A second structure-factor Fourier synthesis was computed to refine our model. The R index, the usual residual based on F(obs), was 0.18 at this point.

Refinement of the structure was continued by full-matrix least-squares methods, using one individual isotropic thermal parameter per atom. After three least-squares cycles, R was reduced to 0.11. The thermal parameters were changed to their anisotropic equivalent, and four additional least-squares cycles reduced R to 0.058. A difference Fourier synthesis was computed and all 12 hydrogen atoms were located. The contributions of the hydrogen atoms were included in all subsequent calculations but their parameters were not varied. An isotropic thermal parameter was assigned to each hydrogen, which was the average

Table I. Final parameters for the non-hydrogen atoms. The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$. All values are X10^4 except for the Cu, Cl and P parameters which are X10^5.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	00000*	19462(3)	25000*	368(5)	117(2)	596(6)	0000*	301(7)	0000*
Cl	—191(8)	12502(4)	40953(9)	882(8)	166(2)	834(9)	—33(6)	494(13)	246(7)
P	12051(5)	30683(3)	8168(7)	266(5)	110(2)	474(7)	— 6(4)	184(8)	—24(5)
O	951(2)	2624(1)	1877(2)	46(2)	18(1)	71(2)	—16(1)	24(3)	13(2)
C1	1956(2)	2644(1)	—313(3)	37(2)	16(1)	58(3)	9(2)	12(4)	—13(2)
CA1	2050(2)	3741(1)	1483(3)	35(2)	12(1)	57(3)	1(2)	19(3)	— 3(2)
CA2	2055(3)	3880(2)	2773(3)	85(3)	23(1)	60(3)	—26(3)	35(5)	— 8(3)
CA3	2743(4)	4369(2)	3343(4)	110(4)	31(1)	73(4)	—31(4)	3(6)	—28(3)
CA4	3435(3)	4714(2)	2637(4)	62(3)	19(1)	117(4)	—14(2)	—37(5)	—13(3)
CA5	3425(3)	4582(2)	1368(4)	45(2)	18(1)	115(4)	—15(2)	23(5)	9(3)
CA6	2743(3)	4098(2)	784(3)	52(2)	19(1)	72(3)	—10(2)	31(4)	0(3)
CB1	—21(2)	3375(2)	—130(3)	33(2)	19(1)	58(3)	9(2)	13(3)	—10(2)
CB2	—133(3)	4027(3)	—528(4)	50(2)	19(1)	109(4)	7(2)	— 5(5)	3(3)
CB3	—1096(3)	4231(2)	—1264(4)	71(3)	24(1)	130(5)	23(3)	—24(6)	13(4)
CB4	—1939(3)	3787(2)	—1597(4)	52(2)	32(1)	95(4)	21(3)	—19(5)	— 6(3)
CB5	—1829(3)	3140(2)	—1213(4)	46(2)	31(1)	88(4)	— 5(3)	—18(4)	—12(3)
CB6	—860(3)	2929(2)	—481(2)	48(2)	22(1)	77(3)	— 4(2)	2(4)	— 2(3)

* Parameter determined by space group symmetry.

Table II. Atomic parameters of hydrogen atoms.

Atom	Bonded to	x	y	z	B
H1	C1	208	298	— 99	2.8
H2	C1	148	233	— 69	2.8
H3	CA2	159	362	327	4.0
H4	CA3	273	445	423	4.8
H5	CA4	395	505	303	4.4
H6	CA5	394	478	91	3.8
H7	CA6	273	402	— 14	3.4
H8	CB2	40	433	— 27	3.8
H9	CB3	—120	470	—146	4.8
H10	CB4	—259	392	—211	4.4
H11	CB5	—243	285	—148	4.3
H12	CB6	— 81	246	— 24	3.7

Table III. Observed and calculated structure amplitudes (X 10) for catena-μ-bis(1,2-diphenylphosphinyl)ethane dichlorocopper(II).

L	FO	FC
H= -14, K= 0		
2	439	-404
4	110	107
H= -12, K= 0		
2	144	138
4	554	534
6	167	-147
8	208	211
H= -10, K= 0		
2	237	289
4	511	547
6	467	-481
8	73	-30
10	268	-259
H= -8, K= 0		
2	392	-388
4	481	462
6	1051	-1110
8	200	-206
10	278	295
H= -6, K= 0		
2	728	-669
4	273	-257
6	1273	-1233
8	1294	1323
10	44	69
12	223	224
H= -4, K= 0		
2	139	119
4	1491	1413
6	156	149
8	440	420
10	186	-190
12	286	260
H= -2, K= 0		
2	2910	2577
4	1177	1102
6	1197	-1148
8	-27	-7
10	307	-293
12	288	283
H= 0, K= 0		
2	85	127
4	494	-468
6	1351	-1298
8	78	75
10	103	-107
12	535	532
H= 2, K= 0		
0	782	627
2	1475	-1360
4	880	762
6	1166	-1096
8	444	441
10	414	436
12	280	265
H= 4, K= 0		
0	1203	1122
2	409	-372
4	341	299
6	847	-797
8	554	561
10	224	-202
H= 6, K= 0		
0	1548	1457
2	62	50
4	1044	1006
6	241	-226
8	76	79
10	251	-249
H= 8, K= 0		
0	1370	1324
2	548	547
4	111	-112
6	974	-1000
8	165	160
H= 10, K= 0		
0	1346	1429
2	326	-340
4	164	-179
6	163	-147
8	160	152
H= 12, K= 0		
0	221	220
2	672	-665
4	304	279
H= 14, K= 0		
0	293	268
2	126	127
H= -13, K= 1		
1	365	-352
2	85	-83
3	337	335
4	163	-157
5	138	142
6	337	-319
7	176	171
H= -11, K= 1		
1	-26	47
2	285	-291
3	530	552
4	114	-96
5	377	-382
6	295	-304
7	89	74
8	85	62
9	116	-104
H= -9, K= 1		
1	679	-714
2	55	-51
3	43	-31
4	163	-153
5	807	-869
6	340	-359
7	376	391
8	115	111
9	235	229
10	-22	53
H= -7, K= 1		
1	1168	-1161
2	526	-490
3	54	-10
4	248	223
5	574	-594
6	203	-192
7	1065	1042
8	-28	4
9	83	89
10	144	-139
11	40	58
H= -5, K= 1		
1	711	-714
2	484	459
3	747	745
4	449	-431
5	283	-305
6	1071	-1027
7	1010	1020
8	-29	-8
9	375	-377
10	98	110
11	128	119
12	278	270
H= -3, K= 1		
1	1108	-1131
2	789	-722
3	782	-669
4	615	-573
5	425	-439
6	737	-660
7	272	284
8	106	116
9	390	-362
10	95	113
11	399	404
12	142	178
H= -1, K= 1		
1	877	-932
2	1982	-1966
3	896	916
4	560	-498
5	937	-916
6	145	-146
7	403	588
8	133	133
9	295	290
10	157	163
11	585	595
12	162	170
H= 1, K= 1		
0	224	139
1	2265	-2442
2	456	429
3	57	28
4	454	416
5	325	-353
6	1072	-975
7	1201	1187
8	228	219
9	481	505
10	68	-68
11	129	122
12	85	85
H= 3, K= 1		
0	828	742
1	1279	-1288
2	122	139
3	1047	1029
4	490	-445
5	261	-276
6	430	-405
7	892	888
8	-27	9
9	392	-400
10	53	65
11	201	-198
H= 5, K= 1		
0	783	710
1	176	101
2	385	-337
3	1053	1042
4	221	-198
5	529	-517
6	418	-401
7	332	340
8	75	-72
9	403	-416
10	131	134
11	201	196
H= 7, K= 1		
0	433	578
1	325	-325
2	617	-582
3	636	-582
4	227	-224
5	794	-840
6	279	-272
7	105	117
8	432	428
9	71	77
10	54	-48
H= 9, K= 1		
0	52	-48
1	975	-1029
2	101	-120
3	47	-26
4	166	168
5	-23	-25
6	-23	-30
7	541	539
8	132	-125
H= 11, K= 1		
0	-25	1
1	585	-630
2	94	96
3	395	402
4	112	100
5	108	112
6	210	-192
7	344	337
H= 13, K= 1		
0	316	488
1	96	97
2	116	-118
3	435	413
4	159	-148
H= -14, K= 2		
1	174	175
2	211	195
3	54	47
4	101	-86
5	493	-499
H= -12, K= 2		
1	433	-437
2	250	241
3	334	-341
4	294	-295
5	384	-329
6	109	-102
7	397	385
8	112	-100
H= -10, K= 2		
1	554	-607
2	114	127
3	-28	-13
4	646	-680
5	140	-148
6	142	157
7	294	305
8	130	120
9	68	-38
10	300	311
H= -8, K= 2		
1	308	-292
2	477	463
3	157	171
4	239	-243
5	377	-386
6	874	908
7	425	452
8	249	-241
9	336	-333
10	95	-111
11	-20	30
H= -6, K= 2		
1	436	-437
2	720	703
3	386	-329
4	63	-74
5	894	-875
6	528	530
7	121	-120
8	546	-546
9	216	213
10	-25	-62
11	351	329
12	112	-109
H= -4, K= 2		
1	1144	-1123
2	844	792
3	478	-390
4	880	-856
5	1077	-1036
6	509	-469
7	756	785
8	950	-959
9	142	130
10	386	394
11	149	142
12	-21	-14
H= -2, K= 2		
1	1770	-1899
2	237	-29
3	1209	-1084
4	1077	-999
5	805	-838
6	335	310
7	895	854
8	74	74
9	105	99
10	502	509
11	-24	-7
12	247	-243
H= 0, K= 2		
0	1553	-1738
1	458	-492
2	578	-558
3	729	-624
4	803	-736
5	560	-553
6	622	592
7	353	347
8	52	75
9	316	-330
10	-24	3
11	103	-113
12	211	-209
H= 2, K= 2		
0	1638	-1369
1	2097	-2195
2	2162	2112
3	459	-368
4	336	-316
5	1075	-1029
6	419	396
7	162	165
8	424	-428
9	62	-78
10	122	-123
11	380	378
12	223	-218
H= 4, K= 2		
0	90	88
1	949	-947
2	1134	1050
3	910	-819
4	708	-669
5	935	-903
6	531	499
7	399	395
8	580	-582
9	300	313
10	211	205
11	177	170
H= 6, K= 2		
0	108	-94
1	1302	-1293
2	314	-295
3	557	-484
4	620	-602
5	195	-205
6	-26	8
7	711	726
8	266	-267
9	43	28
10	270	265
H= 8, K= 2		
0	525	-511
1	490	-493
2	204	191
3	386	398
4	251	-259
5	184	-197
6	196	201
7	57	61
8	90	93
9	147	-133
H= 10, K= 2		
0	765	-823
1	200	-214
2	290	298
3	226	-220
4	-22	-29
5	352	-349
6	199	193
7	85	93
8	269	-263
H= 12, K= 2		
0	-24	-4
1	442	-445
2	346	344
3	173	-171
4	312	-291
5	334	-320
H= 14, K= 2		
0	-19	-13
1	340	-337
H= -13, K= 3		
1	101	100
2	-23	-20
3	218	-201
4	40	21
5	-22	-10
6	417	611
H= -11, K= 3		
1	264	-264
2	647	669
3	534	-559
4	124	131
5	-25	11
6	498	494
7	204	203
8	170	-156
9	219	223
H= -9, K= 3		
1	276	303
2	548	559
3	194	-199
4	-29	-2
5	474	527
6	438	459
7	-26	41
8	569	-593
9	47	42
10	116	114
H= -7, K= 3		
1	448	462
2	390	351
3	953	-888
4	602	-587
5	276	281
6	237	220
7	77	-83
8	-27	20
9	902	901
10	503	490
11	82	81
H= -5, K= 3		
1	178	-148
2	33	12
3	646	-478
4	537	-513
5	93	69
6	1417	1372
7	167	-163
8	457	464
9	422	446
10	100	93
11	132	-132
12	397	-399
H= -3, K= 3		
1	813	-747
2	1278	1227
3	600	-629
4	1033	972
5	981	952
6	1697	1620
7	378	409
8	540	-548
9	606	418
10	-24	-11
11	182	-182
12	359	-360
H= -1, K= 3		
1	565	578
2	2165	2206
3	178	-186
4	130	-121
5	485	-400
6	473	614
7	271	228
8	505	-490
9	157	159
10	71	-93
11	247	-258
12	166	-156
H= 1, K= 3		
0	602	663
1	1546	1567
2	151	-156
3	1244	-1185
4	550	-506
5	613	573
6	741	686
7	172	-176
8	266	-265
9	108	117
10	370	364
11	109	-116
12	-20	-40
H= 3, K= 3		
0	2879	-3085
1	48	54
2	883	789
3	1442	-1358
4	265	-245
5	179	192
6	740	703
7	-26	-13
8	65	73
9	515	511
10	285	283
11	202	203
H= 5, K= 3		
0	862	-808
1	845	-730
2	341	306
3	890	-854
4	47	49
5	472	433
6	1155	1134
7	309	296
8	116	-116
9	268	273
10	96	-109
11	235	-232
H= 7, K= 3		
0	654	-625
1	140	135
2	862	844
3	135	135
4	206	222
5	552	598
6	352	352
7	55	-67
8	316	-309
9	245	240
10	-17	-13
H= 9, K= 3		
0	185	-169
1	323	352
2	621	656
3	144	144
4	378	-383
5	-23	-31
6	76	76
7	92	-93
8	120	-105
H= 11, K= 3		
0	298	-308
1	398	411
2	71	-94
3	439	-434
4	226	-218
5	135	-119
6	478	459
H= 13, K= 3		
0	492	-463
1	76	75
2	156	148
3	303	-299
4	149	142
H= -14, K= 4		
1	79	46
2	-20	-14
3	158	-151
4	-19	2
H= -12, K= 4		
1	532	556
2	451	-453
3	126	127
4	95	-85
5	449	437
6	178	170
7	449	-440
8	36	3
H= -10, K= 4		
1	669	721
2	61	-77
3	338	-370
4	335	363
5	42	-42
6	122	123
7	544	-562
8	155	-158
9	337	313
10	90	-88
H= -8, K= 4		
1	-26	18
2	867	-850
3	1086	-1126
4	72	37
5	270	272
6	-29	24
7	93	87
8	253	233
9	445	430
10	144	-140
11	172	-182
H= -6, K= 4		
1	348	349
2	880	-836
3	323	-354
4	479	432
5	844	866
6	95	65
7	360	-376
8	-28	23
9	368	366
10	224	-221
11	358	-353
H= -4, K= 4		
1	1325	1338
2	196	159
3	270	-324
4	192	199
5	699	683
6	401	399
7	551	-550
8	682	689
9	91	-83
10	300	-303
11	329	-313
12	123	-136
H= -2, K= 4		
1	775	862
2	1404	-1507
3	1545	-1575
4	88	-16
5	161	193
6	968	892
7	758	-770
8	245	-234
9	372	376
10	393	-404
11	89	96
12	-20	-35
H= 0, K= 4		
0	1229	-1216
1	1321	1433
2	663	-629
3	1188	-1217
4	983	929
5	464	472
6	354	337
7	235	-231
8	45	-41
9	797	825
10	140	-144
11	66	-71
12	163	-155
H= 2, K= 4		
0	464	-420
1	1138	-1026
2	1384	-1281
3	849	-871
4	409	382
5	1277	1253
6	52	45
7	-26	-5
8	306	315
9	324	325
10	164	-160
11	360	-354
12	69	-72
H= 4, K= 4		
0	2193	-2112
1	1381	1390
2	1068	-983
3	609	484
4	557	535
5	676	683
6	371	341
7	514	-519
8	182	-169
9	186	-197
10	136	-145
11	344	-337
H= 6, K= 4		
0	929	-835
1	1537	1519
2	55	33
3	857	-846
4	261	281
5	183	-168
6	-26	27
7	591	-603
8	428	436
9	253	249
10	199	-197
H= 8, K= 4		
0	292	-290
1	151	177
2	359	-382
3	946	-1014
4	-26	46
5	-24	29
6	316	300
7	138	-139
8	67	-63
9	434	434
H= 10, K= 4		
0	360	-371
1	318	-339
2	71	-48
3	377	-408
4	202	212
5	651	654
6	84	79
7	222	215
H= 12, K= 4		
0	45	42
1	374	376
2	215	-215
3	140	140
4	107	99
5	295	289
H= 14, K= 4		
0	214	-197
1	478	459
H= -13, K= 5		
1	192	188
2	143	-131
3	152	-144
4	310	290
5	-21	-2
6	360	-347
H= -11, K= 5		
1	144	-153
2	431	-433
3	205	212
4	44	24
5	344	382
6	424	-420
7	207	-215
8	485	472
9	61	22
H= -9, K= 5		
1	67	40
2	880	-917
3	380	383
4	482	520
5	-29	24
6	337	345
7	128	-144
8	538	532
9	172	-167
10	291	-300
H= -7, K= 5		
1	705	694
2	199	-202
3	215	214
4	1201	1208
5	96	-93
6	133	134
7	243	-250
8	204	192
9	274	-260
10	733	-745
11	143	-156
H= -5, K= 5		
1	580	566
2	528	-487
3	266	238
4	1398	1340
5	146	149
6	601	-591
7	243	-236
8	214	-215
9	80	-92
10	641	-684
11	-23	-13
12	179	184
H= -3, K= 5		
1	429	-377
2	931	-915
3	396	-382
4	40	-7
5	473	446
6	935	-900
7	189	-194
8	288	244
9	438	-456
10	-26	30
11	-23	-10
12	197	188
H= -1, K= 5		
1	1065	1112
2	2013	-2069
3	1041	934
4	976	959
5	602	574
6	-25	0
7	508	-518
8	958	972
9	41	-34
10	495	-490
11	172	-183
12	76	-89
H= 1, K= 5		
0	326	-318
1	507	514
2	1436	-1378
3	851	771
4	1482	1409
5	192	194
6	227	204
7	485	-478
8	274	269
9	127	-131
10	636	-643
11	115	-109
12	79	-82
H= 3, K= 5		
0	623	586
1	68	-5
2	602	705
3	730	639
4	1335	1245
5	281	-265
6	440	-435
7	352	-365
8	89	-108
9	154	-163
10	535	-534
11	122	-115
H= 5, K= 5		
0	1085	1045
1	899	847
2	1273	-1219
3	192	-187
4	283	281
5	87	90
6	389	-390
7	215	220
8	155	143
9	165	-162
10	162	-158
H= 7, K= 5		
0	285	259
1	55	79
2	861	-840
3	47	37
4	365	370
5	195	216
6	321	-334
7	381	-387
8	239	230
9	160	-153
H= 9, K= 5		
0	229	-240
1	292	320
2	477	-512
3	212	242
4	505	497
5	122	143
6	-22	40
7	221	-227
8	318	304
H= 11, K= 5		
0	280	265
1	-23	-1
2	161	-158
3	51	-46
4	348	341
5	54	-58
6	189	-189
H= 13, K= 5		
0	311	298
1	84	82
2	112	-99
3	34	44
H= -14, K= 6		
1	58	52
2	274	-270
3	234	242
H= -12, K= 6		
1	248	-256
2	176	-158
3	91	92
4	367	364
5	313	-320
6	80	44
7	263	294
H= -10, K= 6		
1	719	-780
2	133	148
3	520	551
4	324	341
5	165	183
6	144	-154
7	402	410
8	-23	-13
9	535	-531
H= -8, K= 6		
1	191	189
2	97	92
3	1059	1122
4	87	78
5	79	79
6	321	-318
7	82	-84
8	151	148
9	354	-350
10	-22	-7
H= -6, K= 6		
1	57	35
2	448	-442
3	1081	1079
4	77	67
5	576	-601
6	-28	12
7	102	-104
8	320	318
9	362	-367
10	170	180
11	318	323
H= -4, K= 6		
1	755	-782
2	1118	-1059
3	1220	1205
4	516	470
5	215	-235
6	186	157
7	191	199
8	445	417
9	275	-274
10	192	-183
11	235	235
12	75	-77
H= -2, K= 6		
1	373	-419
2	90	72
3	1609	1632
4	1415	1519
5	182	-178
6	137	-135
7	583	600
8	51	-53
9	550	-559
10	145	-156
11	58	-43
12	130	134
H= 0, K= 6		
0	470	-479
1	457	400
2	198	-194
3	1721	1726
4	417	383
5	296	-318
6	640	-600
7	-24	-23
8	320	351
9	895	-937
10	-24	-11
11	42	-36
12	227	224
H= 2, K= 6		
0	996	928
1	295	221
2	150	-134
3	1489	1452
4	64	-83
5	166	-198
6	201	-214
7	519	-528
8	584	380
9	433	-455
10	57	-39
11	466	454
H= 4, K= 6		
0	30	-67
1	892	-861
2	148	-135
3	569	587
4	522	477
5	704	-732
6	416	429
7	485	511
8	321	324
9	99	-97
10	67	65
11	278	285
H= 6, K= 6		
0	868	797
1	262	-318
2	446	-436
3	895	905
4	347	375
5	265	252
6	-25	-19
7	275	273
8	98	94
9	179	-176
10	201	-190
H= 8, K= 6		
0	458	464
1	49	41
2	39	-16
3	1141	1252
4	617	643
5	94	76
6	123	-126
7	-22	-9
8	-20	-30
9	360	-361
H= 10, K= 6		
0	-25	34
1	124	139
2	117	-110
3	479	498
4	39	-52
5	428	-437
6	178	-163
7	112	-112
H= 12, K= 6		
0	70	72
1	-23	11
2	91	-82
3	-21	9
4	174	165
5	266	-264
H= 14, K= 6		
0	81	79
H= -13, K= 7		
1	-21	-19
2	90	92
3	539	512
4	213	-208
5	43	-13
H= -11, K= 7		
1	190	142
2	303	308
3	591	605
4	71	-75
5	295	-306
6	75	79
7	315	-320
8	487	-482
H= -9, K= 7		
1	-27	-3
2	624	663
3	-28	24
4	364	-382
5	327	-579
6	270	-287
7	275	287
8	363	-364
9	181	-186
10	198	210
H= -7, K= 7		
1	643	-675
2	124	-95
3	310	303
4	928	-980
5	72	61
6	253	-266
7	281	271
8	274	-265
9	208	-221
10	337	341
11	151	164
H= -5, K= 7		
1	439	-478
2	345	342
3	1216	1230
4	244	-266
5	53	6
6	110	137
7	236	-236
8	100	-93
9	369	-378
10	298	306
11	60	-50
H= -3, K= 7		
1	116	-170
2	1333	1333
3	1793	1786
4	889	-813
5	742	-735
6	324	321
7	56	75
8	257	-259
9	690	-709
10	-24	10
11	247	245
12	52	-47
H= -1, K= 7		
1	-22	-69
2	1318	1324
3	275	327
4	425	-410
5	994	-975
6	307	-292
7	-27	-18
8	922	-950
9	131	-129
10	203	203
11	391	386
12	-19	28
H= 1, K= 7		
0	1043	970
1	331	215
2	647	640
3	413	463
4	1320	-1289
5	434	-438
6	444	-417
7	376	399
8	190	-103
9	195	-204
10	354	363
11	235	239
H= 3, K= 7		
0	153	-155
1	1424	-1480
2	619	-545
3	1062	1090
4	843	-807
5	445	649
6	151	172
7	263	288
8	367	-368
9	461	-476
10	167	194
11	-19	2
H= 5, K= 7		
0	1133	-1102
1	373	334
2	746	751
3	741	790
4	145	-175
5	483	-504
6	83	-107
7	377	-369
8	135	-143
9	414	-409
10	114	112
H= 7, K= 7		
0	184	173
1	128	-136
2	719	716
3	523	595
4	407	-443
5	532	-595
6	49	-53
7	44	-24
8	269	-258
9	78	81
H= 9, K= 7		
0	76	76
1	661	-740
2	199	221
3	34	-17
4	484	-509
5	202	-200
6	100	-96
7	309	310
8	218	-201
H= 11, K= 7		
0	61	65
1	133	-154
2	78	74
3	405	408
4	371	-371
5	41	44
6	77	68
H= 13, K= 7		
0	305	-280
1	120	126
2	87	-36
3	283	289
H= -12, K= 8		
1	254	245
2	399	330
3	54	59
4	676	-649
5	144	137
6	234	-225
7	270	-262
H= -10, K= 8		
1	61	-64
2	53	-51
3	85	82
4	589	-624
5	150	120
6	260	254
7	94	-94
8	-22	-25
9	132	114
H= -8, K= 8		
1	223	254
2	419	419
3	327	-350
4	166	-165
5	151	-174
6	297	311
7	143	-138
8	249	-251
9	128	129
10	311	317
H= -6, K= 8		
1	365	344
2	1466	1432
3	133	-106
4	262	-257
5	220	234
6	292	-295
7	-29	46
8	665	-649
9	-25	32
10	51	-41
11	162	-176
H= -4, K= 8		
1	67	-40
2	1201	1252
3	439	-394
4	1373	-1351
5	284	274
6	342	-340
7	298	-284
8	589	-594
9	-24	15
10	547	539
11	-21	35
H= -2, K= 8		
1	350	362
2	427	423
3	202	-168
4	2207	-2151
5	330	303
6	109	-83
7	246	-255
8	105	-99
9	-24	-25
10	616	626
11	-22	-9
H= 0, K= 8		
0	326	-311
1	498	473
2	164	178
3	140	-139
4	402	-371
5	147	173
6	697	669
7	98	-89
8	293	-304
9	429	444
10	251	247
11	-22	-21
H= 2, K= 8		
0	250	-221
1	114	131
2	1414	1388
3	211	194
4	266	-259
5	372	360
6	-26	-1
7	255	-271
8	741	-759
9	-24	26
10	310	306
11	252	-244
H= 4, K= 8		
0	676	647
1	347	291
2	1253	1245
3	89	75
4	1072	-1053
5	62	47
6	690	-676
7	106	111
8	257	-268
9	189	-181
10	243	229
H= 6, K= 8		
0	68	52
1	685	693
2	297	303
3	255	-255
4	997	-1028
5	-26	4
6	104	100
7	334	-345
8	138	-127
9	-20	-6
10	376	376
H= 8, K= 8		
0	730	-773
1	39	45
2	198	187
3	296	-310
4	492	-522
5	90	96
6	184	179
7	180	-176
8	-19	12
H= 10, K= 8		
0	69	77
1	-24	-26
2	414	420
3	-23	14
4	176	-176
5	130	109
6	307	293
7	40	45
H= 12, K= 8		
0	50	39
1	154	147
2	449	416
3	-19	-9
4	98	-96
H= -13, K= 9		
1	318	294
2	99	94
3	633	-624
4	57	42
H= -11, K= 9		
1	92	-98
2	-24	2
3	563	-585
4	-24	-6
5	450	447
6	61	39
7	124	120
8	81	72
H= -9, K= 9		
1	180	-182
2	329	339
3	208	-226
4	226	-230
5	494	327
6	245	-250
7	178	-175
8	127	136
9	148	136
H= -7, K= 9		
1	1186	1233
2	190	181
3	254	-273
4	135	-65
5	88	-84
6	73	88
7	563	-561
8	-25	-4
9	237	242
10	180	176
H= -5, K= 9		
1	436	472
2	48	-7
3	1464	-1443
4	74	-81
5	79	76
6	187	-221
7	136	-152
8	68	-72
9	684	692
10	335	342
11	181	186
H= -3, K= 9		
1	117	138
2	249	199
3	1421	-1435
4	216	-213
5	173	225
6	274	-288
7	54	-55
8	181	190
9	595	597
10	-24	29
11	137	-141
H= -1, K= 9		
1	388	439
2	220	177
3	1300	-1265
4	-23	12
5	993	991
6	309	-289
7	84	57
8	-28	34
9	264	274
10	464	473
11	477	-470
H= 1, K= 9		
0	175	176
1	346	409
2	747	680
3	601	-609
4	442	-437
5	302	315
6	303	-318
7	527	-995
8	318	341
9	258	279
10	-23	40
11	-19	-19
H= 3, K= 9		
0	1108	1099
1	239	273
2	92	-93
3	1009	-1037
4	61	-71
5	394	-397
6	361	364
7	217	-230
8	54	54
9	508	520
10	199	186
11	60	74
H= 5, K= 9		
0	107	119
1	88	92
2	586	556
3	1283	-1375
4	57	-12
5	187	215
6	186	-188
7	346	359
8	68	84
9	593	597
10	204	198
H= 7, K= 9		
0	637	680
1	265	285
2	-28	-24
3	437	-482
4	-25	37
5	671	710
6	40	-36
7	69	-57
8	-20	0
9	107	105
H= 9, K= 9		
0	184	190
1	430	467
2	100	104
3	198	-203
4	-23	27
5	228	243
6	41	-40
7	340	-320
H= 11, K= 9		
0	69	70
1	204	200
2	101	101
3	423	-415
4	143	-123
5	119	-122
H= 13, K= 9		
0	125	113
1	127	-120
H= -12, K= 10		
1	67	66
2	174	-169
3	73	-74
4	560	537
5	-20	43
6	53	55
H= -10, K= 10		
1	116	131
2	131	-142
3	370	-383
4	361	398
5	172	-170
6	433	-422
7	91	-88
8	-21	0
H= -8, K= 10		
1	63	-45
2	95	103
3	641	-705
4	48	-57
5	-26	4
6	663	-704
7	337	347
8	65	78
9	391	372
10	111	-106
H= -6, K= 10		
1	265	-247
2	1187	-1233
3	617	-639
4	-27	-30
5	372	395
6	219	-219
7	111	74
8	622	613
9	445	445
10	88	94
H= -4, K= 10		
1	183	-152
2	1041	-1030
3	213	-222
4	794	772
5	45	45
6	-28	48
7	106	115
8	317	309
9	251	257
10	353	-349
11	148	-150
H= -2, K= 10		
1	133	-96
2	178	122
3	403	-438
4	1166	1164
5	175	-142
6	446	-452
7	195	195
8	134	123
9	216	225
10	451	-452
11	38	52
H= 0, K= 10		
0	1289	1284
1	339	350
2	129	-143
3	1273	-1279
4	233	221
5	257	-243
6	1264	-1263
7	40	23
8	78	85
9	507	534
10	150	-137
11	96	94
H= 2, K= 10		
0	571	597
1	234	-183
2	1119	-1089
3	708	-725
4	312	-289
5	246	265
6	258	-249
7	481	514
8	308	335
9	328	336
10	145	-143
11	123	-120
H= 4, K= 10		
0	265	290
1	558	-505
2	889	-883
3	708	-695
4	320	344
5	352	394
6	216	-225
7	109	101
8	443	450
9	134	134
10	161	-163
H= 6, K= 10		
0	316	334
1	279	306
2	286	-279
3	180	-178
4	557	570
5	46	-46
6	192	-209
7	84	-87
8	106	-112
9	204	199
H= 8, K= 10		
0	645	682
1	238	-251
2	214	-227
3	313	-348
4	253	268
5	70	82
6	491	-477
7	114	112
8	52	-29
H= 10, K= 10		
0	418	425
1	67	-56
2	381	-387
3	206	-205
4	127	-129
5	65	-49
6	345	-332
H= 12, K= 10		
0	100	-105
1	148	143
2	403	-374
3	110	-94
H= -13, K= 11		
1	201	-183
2	62	-59
H= -11, K= 11		
1	94	98
2	495	-499
3	187	183
4	104	-110
5	471	-448
6	75	-61
7	141	137
H= -9, K= 11		
1	379	-389
2	689	-738
3	145	-155
4	262	273
5	347	-347
6	117	117
7	302	292
8	405	397
9	-19	-11
H= -7, K= 11		
1	650	-678
2	330	-350
3	219	-243
4	675	704
5	192	-207
6	-25	-29
7	515	529
8	191	180
9	53	65
10	344	-343
H= -5, K= 11		
1	835	-854
2	157	-152
3	305	332
4	310	321
5	163	-163
6	190	-198
7	309	313
8	91	91
9	259	-256
10	337	-322
H= -3, K= 11		
1	492	-673
2	834	-734
3	470	467
4	-26	-19
5	614	-606
6	97	-81
7	228	220
8	634	437
9	-24	-21
10	61	-65
11	98	101
H= -1, K= 11		
1	570	-567
2	1265	-1199
3	340	-344
4	147	132
5	916	-925
6	249	238
7	675	696
8	500	495
9	71	-48
10	138	-141
11	243	233
H= 1, K= 11		
0	498	-476
1	888	-877
2	683	-648
3	196	-183
4	1294	1269
5	48	-35
6	438	454
7	540	574
8	-23	10
9	127	115
10	337	-329
11	36	-42
H= 3, K= 11		
0	90	97
1	718	-737
2	551	-551
3	299	313
4	431	416
5	42	48
6	391	-407
7	496	526
8	187	188
9	338	-340
10	159	-155
H= 5, K= 11		
0	260	265
1	401	-413
2	242	-250
3	458	485
4	124	121
5	438	-482
6	186	-199
7	117	-122
8	236	226
9	258	-252
H= 7, K= 11		
0	658	-708
1	87	-74
2	643	-706
3	196	-217
4	263	266
5	504	-521
6	151	169
7	115	114
8	342	328
H= 9, K= 11		
0	-25	-15
1	797	-843
2	232	-231
3	130	-141
4	213	212
5	223	-235
6	182	192
7	407	387
H= 11, K= 11		
0	138	123
1	271	-262
2	-21	3
3	200	198
4	453	441
H= -12, K= 12		
1	345	-332
2	70	59
3	113	-108
4	66	-43
H= -10, K= 12		
1	506	-319
2	67	-62
3	410	422
4	-24	-16
5	157	157
6	472	470
7	365	350
H= -8, K= 12		
1	140	-162
2	193	201
3	759	811
4	205	210
5	370	-382
6	554	549
7	79	86
8	121	114
9	439	-434
H= -6, K= 12		
1	342	347
2	220	225
3	43	63
4	469	491
5	530	-561
6	545	579
7	134	136
8	311	-317
9	194	-190
10	87	-88
H= -4, K= 12		
1	911	-948
2	662	664
3	56	-45
4	62	-25
5	391	-410
6	279	268
7	465	487
8	53	-25
9	44	-33
10	69	-64
H= -2, K= 12		
1	728	-773
2	254	-229
3	358	363
4	354	-348
5	120	-120
6	692	702
7	565	580
8	75	81
9	226	-232
10	-22	16
H= 0, K= 12		
0	1190	-1192
1	408	-416
2	343	331
3	814	830
4	370	336
5	290	262
6	701	734
7	-25	14
8	60	-60
9	368	-379
10	63	62
H= 2, K= 12		
0	407	-430
1	375	-388
2	-24	-16
3	633	641
4	422	402
5	1015	-1077
6	822	875
7	-25	-25
8	38	-47
9	180	-177
10	171	-176
H= 4, K= 12		
0	357	-374
1	398	-444
2	338	351
3	106	-96
4	265	261
5	531	-570
6	184	203
7	448	459
8	225	-213
9	-21	36
H= 6, K= 12		
0	631	-648
1	853	-901
2	497	552
3	-26	14
4	-24	47
5	75	69
6	189	206
7	533	549
8	107	101
H= 8, K= 12		
0	303	-310
1	136	-125
2	112	-125
3	440	485
4	140	-151
5	-22	27
6	462	441
7	44	-38
H= 10, K= 12		
0	232	-226
1	-22	4
2	214	211
3	258	267
4	172	166
5	280	-265
H= 12, K= 12		
0	56	-58
1	346	-342
2	112	111
H= -11, K= 13		
1	-21	-21
2	301	287
3	-22	38
4	98	110
5	109	104
6	415	408
H= -9, K= 13		
1	41	-52
2	353	371
3	166	181
4	311	-302
5	176	168
6	87	72
7	94	-91
8	562	-551
H= -7, K= 13		
1	67	79
2	440	481
3	210	230
4	561	-587
5	261	255
6	177	174
7	-24	-11
8	167	-151
9	47	-93
H= -5, K= 13		
1	524	515
2	630	-653
3	290	300
4	533	-554
5	238	251
6	880	907
7	75	-42
8	-24	4
9	69	-68
10	115	102
H= -3, K= 13		
1	170	163
2	277	279
3	196	197
4	490	485
5	316	324
6	835	849
7	61	-43
8	513	-516
9	161	-166
10	225	-228
H= -1, K= 13		
1	502	462
2	1122	1112
3	411	410
4	111	-97
5	389	394
6	-26	17
7	311	-316
8	351	-348
9	204	-198
10	61	-68
H= 1, K= 13		
0	824	-830
1	172	139
2	85	94
3	273	275
4	758	-777
5	227	223
6	291	310
7	162	-164
8	533	-337
9	63	44
10	169	173
H= 3, K= 13		
0	1235	-1263
1	294	272
2	95	106
3	270	282
4	482	-500
5	121	124
6	548	572
7	52	-52
8	144	156
9	109	-110
H= 5, K= 13		
0	767	-774
1	293	300
2	107	108
3	412	470
4	122	-121
5	267	285
6	629	654
7	44	15
8	211	-205
9	31	-2
H= 7, K= 13		
0	606	-647
1	435	447
2	392	410
3	-23	7
4	99	117
5	236	244
6	225	220
7	67	-61
H= 9, K= 13		
0	126	-117
1	232	240
2	218	209
3	299	321
4	315	-301
5	174	150
6	57	-62
H= 11, K= 13		
0	576	-541
1	125	131
2	174	-155
3	54	56
H= -10, K= 14		
1	747	736
2	-22	-27
3	239	-230
4	219	-213
5	118	-116
6	38	-40
H= -8, K= 14		
1	103	113
2	89	-70
3	329	-333
4	78	-70
5	456	446
6	40	34
7	280	-271
8	-20	27
H= -6, K= 14		
1	180	193
2	135	125
3	235	-248
4	-25	-1
5	583	591
6	152	161
7	372	-351
8	281	-275
9	53	-73
H= -4, K= 14		
1	730	758
2	42	-57
3	584	609
4	59	-43
5	537	566
6	70	-51
7	792	-812
8	174	-169
9	242	-245
10	-19	3
H= -2, K= 14		
1	1092	1088
2	59	9
3	102	-89
4	-27	5
5	175	-174
6	81	-83
7	648	-655
8	81	80
9	-22	41
10	135	121
H= 0, K= 14		
0	625	-598
1	584	587
2	231	208
3	557	-580
4	112	-100
5	298	307
6	170	170
7	477	-469
8	112	-107
9	42	35
10	73	-62
H= 2, K= 14		
0	44	46
1	511	526
2	-25	26
3	259	-257
4	-26	33
5	713	762
6	-23	10
7	115	-114
8	121	-120
9	104	94
H= 4, K= 14		
0	59	74
1	602	634
2	-26	2
3	319	337
4	172	-190
5	470	493
6	67	54
7	674	-692
8	114	-107
9	317	-317
H= 6, K= 14		
0	373	-394
1	742	818
2	-24	-19
3	52	-55
4	-23	17
5	-23	-19
6	54	-82
7	707	-688
8	74	-62

Table III. (continued)

L	FO	FC
H= 8, K= 14		
0	76	-75
1	252	260
2	-23	1
3	453	-472
4	-21	-24
5	47	-48
6	171	163
H= 10, K= 14		
0	78	-67
1	133	-142
2	59	50
3	157	-133
4	93	86
H= -11, K= 15		
1	55	-51
2	284	-267
3	93	-86
4	85	65
H= -9, K= 15		
1	377	374
2	250	-240
3	389	375
4	388	372
5	310	286
6	-20	-20
7	168	-164
H= -7, K= 15		
1	410	433
2	134	130
3	41	33
4	555	559
5	97	118
6	325	-322
7	391	-377
8	39	33
H= -5, K= 15		
1	350	395
2	474	493
3	253	-263
4	469	483
5	84	90
6	611	-615
7	387	-403
8	84	-99
9	106	107
H= -3, K= 15		
1	149	-144
2	226	-235
3	169	153
4	351	-365
5	179	187
6	612	-629
7	-25	29
8	325	313
9	172	160
H= -1, K= 15		
1	442	446
2	474	-497
3	304	294
4	171	190
5	504	521
6	221	-225
7	322	-337
8	231	222
9	77	-75
H= 1, K= 15		
0	560	572
1	749	787
2	103	-87
3	313	310
4	725	746
5	249	248
6	87	-91
7	283	-280
8	79	67
9	136	-160
H= 3, K= 15		
0	1169	1245
1	579	631
2	131	125
3	62	-74
4	374	380
5	125	-119
6	625	-653
7	355	-359
8	-21	-50
9	85	88
H= 5, K= 15		
0	889	951
1	-25	-20
2	-24	27
3	176	-177
4	81	97
5	254	270
6	630	-638
7	96	-84
8	200	189
H= 7, K= 15		
0	334	347
1	-23	17
2	220	-202
3	176	170
4	137	-152
5	302	302
6	71	-70
7	121	-100
H= 9, K= 15		
0	271	286
1	484	491
2	296	-285
3	231	210
4	271	259
5	-17	13
H= 11, K= 15		
0	507	487
1	242	218
H= -10, K= 16		
1	345	-322
2	-20	3
3	221	200
4	135	123
H= -8, K= 16		
1	266	-266
2	273	-248
3	368	396
4	74	-68
5	124	-117
6	687	-667
7	38	-47
H= -6, K= 16		
1	60	82
2	183	-180
3	325	326
4	326	-336
5	367	-377
6	591	-969
7	171	159
8	331	333
H= -4, K= 16		
1	119	-124
2	729	-773
3	64	-83
4	162	160
5	328	-326
6	55	-61
7	256	258
8	188	178
9	69	67
H= -2, K= 16		
1	348	-367
2	348	359
3	193	200
4	288	268
5	43	-24
6	845	-840
7	130	125
8	52	-59
9	162	-162
H= 0, K= 16		
0	1106	1114
1	395	-391
2	184	-183
3	504	543
4	381	-399
5	67	-48
6	535	-542
7	76	65
8	46	10
9	144	-145
H= 2, K= 16		
0	453	448
1	222	-229
2	681	-707
3	138	137
4	142	-142
5	467	-476
6	538	-552
7	65	-64
8	201	188
9	78	-62
H= 4, K= 16		
0	234	240
1	231	-228
2	316	-315
3	389	403
4	96	88
5	373	-379
6	209	-190
7	240	239
8	415	395
H= 6, K= 16		
0	313	324
1	240	-245
2	66	-41
3	-23	16
4	231	230
5	-21	39
6	205	-181
7	315	316
H= 8, K= 16		
0	470	469
1	45	43
2	116	127
3	242	223
4	-19	-23
5	37	33
H= 10, K= 16		
0	523	490
1	-19	-5
2	421	-398
H= -9, K= 17		
1	253	-239
2	300	269
3	113	-121
4	305	-302
5	410	-390
H= -7, K= 17		
1	684	-690
2	90	100
3	83	-77
4	366	-361
5	226	-220
6	-21	15
7	473	484
H= -5, K= 17		
1	348	-359
2	83	87
3	138	155
4	209	-218
5	117	-118
6	72	63
7	370	351
8	121	-129
H= -3, K= 17		
1	79	-81
2	115	128
3	396	367
4	54	-62
5	603	-606
6	174	-173
7	-22	-27
8	-20	11
H= -1, K= 17		
1	490	-499
2	496	530
3	228	-226
4	87	-97
5	617	-660
6	70	-74
7	72	65
8	112	-124
9	95	95
H= 1, K= 17		
0	77	66
1	788	-844
2	322	390
3	300	-325
4	564	-585
5	446	-476
6	302	-304
7	500	504
8	62	-49
H= 3, K= 17		
0	432	441
1	598	-625
2	116	143
3	210	214
4	320	-328
5	163	-163
6	75	80
7	432	408
8	46	-46
H= 5, K= 17		
0	201	-206
1	176	-173
2	-23	0
3	251	258
4	171	-175
5	245	-244
6	55	-45
7	70	-57
H= 7, K= 17		
0	304	287
1	265	-273
2	294	285
3	137	-145
4	198	-198
5	479	-494
H= 9, K= 17		
0	105	89
1	560	-520
2	-18	-3
3	170	-195
H= -8, K= 18		
1	53	51
2	200	185
3	134	-134
4	76	-65
5	105	94
H= -6, K= 18		
1	330	-351
2	757	746
3	291	-282
4	-23	-22
5	41	-19
6	225	204
7	38	6
H= -4, K= 18		
1	67	-62
2	369	381
3	301	-291
4	461	-460
5	222	-224
6	88	74
7	257	250
8	252	-227
H= -2, K= 18		
1	317	-339
2	72	16
3	138	-134
4	566	-579
5	56	40
6	256	247
7	304	298
8	178	176
H= 0, K= 18		
0	812	-805
1	75	-83
2	130	140
3	360	-350
4	59	-54
5	-23	-21
6	602	662
7	321	313
8	-18	14
H= 2, K= 18		
0	310	-309
1	125	120
2	803	827
3	183	-176
4	-23	-22
5	190	180
6	264	259
7	196	193
H= 4, K= 18		
0	242	244
1	175	-167
2	451	442
3	242	-248
4	303	-283
5	85	-95
6	-19	-20
7	31	0
H= 6, K= 18		
0	182	-184
1	171	-185
2	36	51
3	150	-155
4	511	-500
5	37	34
H= 8, K= 18		
0	534	-504
1	195	-151
2	76	72
3	61	-42
H= -9, K= 19		
1	109	92
H= -7, K= 19		
1	451	418
2	190	-146
3	238	-217
4	188	-175
5	119	98
H= -5, K= 19		
1	144	126
2	-23	-46
3	731	-718
4	168	-159
5	38	-45
6	359	342
7	-17	28
H= -3, K= 19		
1	-23	0
2	166	-170
3	650	-657
4	163	164
5	277	270
6	219	213
7	-19	16
H= -1, K= 19		
1	41	-57
2	189	179
3	219	-222
4	267	-268
5	455	437
6	127	135
7	57	42
H= 1, K= 19		
0	202	-198
1	498	505
2	292	-327
3	398	-398
4	146	-136
5	113	106
6	306	299
7	273	-261
H= 3, K= 19		
0	614	-661
1	261	261
2	309	-334
3	615	-610
4	98	108
5	93	-100
6	126	121
7	111	-112
H= 5, K= 19		
0	457	-443
1	194	-197
2	117	107
3	641	-616
4	122	130
5	189	182
H= 7, K= 19		
0	317	-307
1	38	-15
2	216	202
3	208	-176
4	-17	3
H= -8, K= 20		
1	125	-110
2	130	-127
H= -6, K= 20		
1	-20	1
2	503	-482
3	-21	-13
4	187	181
5	498	477
H= -4, K= 20		
1	464	466
2	253	-249
3	87	-89
4	461	448
5	195	188
6	105	111
H= -2, K= 20		
1	393	394
2	260	-262
3	96	-95
4	612	595
5	142	136
6	192	189
7	388	-395
H= 0, K= 20		
0	75	58
1	39	-43
2	77	-72
3	434	-440
4	335	334
5	98	91
6	196	-189
7	-17	-32
H= 2, K= 20		
0	96	105
1	164	-173
2	396	-361
3	155	-154
4	76	55
5	175	159
6	39	-27
H= 4, K= 20		
0	231	-221
1	302	303
2	519	-516
3	113	104
4	448	439
5	341	328
H= 6, K= 20		
0	72	-66
1	389	362
2	87	3
3	64	-60
4	293	282
H= 8, K= 20		
0	266	250
H= -7, K= 21		
1	237	-214
2	73	-55
H= -5, K= 21		
1	147	-127
2	113	-103
3	372	365
4	290	289
5	61	-43
H= -3, K= 21		
1	179	195
2	365	-351
3	310	295
4	340	311
5	-19	19
6	202	-187
H= -1, K= 21		
1	177	-161
2	536	-526
3	327	320
4	267	261
5	96	-76
6	143	150
H= 1, K= 21		
0	191	-200
1	68	-64
2	110	-110
3	214	215
4	512	486
5	56	41
6	180	178
H= 3, K= 21		
0	225	213
1	-21	-12
2	44	62
3	449	433
4	449	434
5	103	116
H= 5, K= 21		
0	302	292
1	107	111
2	373	-357
3	288	286
H= 7, K= 21		
0	134	-126
H= -6, K= 22		
1	-17	2
H= -4, K= 22		
1	347	-322
2	147	133
3	210	194
4	-18	-10
H= -2, K= 22		
1	372	-355
2	173	-149
3	522	498
4	-18	-18
5	-18	13
H= 0, K= 22		
0	73	-68
1	-21	42
2	134	131
3	673	648
4	130	-130
5	47	-43
H= 2, K= 22		
0	103	-106
1	296	306
2	-20	3
3	457	436
4	63	59
H= 4, K= 22		
0	-19	-21
1	247	-238
2	60	52
3	55	-53
H= 6, K= 22		
0	35	-19
H= -3, K= 23		
1	219	208
2	444	437
3	150	149
H= -1, K= 23		
1	106	89
2	387	370
3	177	176
H= 1, K= 23		
0	193	205
1	116	-117
2	355	358
3	85	85
H= 3, K= 23		
0	292	-268
1	-18	5
2	155	-130
H= 0, K= 24		
0	46	41
1	42	16

value for the carbon atom to which it was bonded. Two additional full-matrix least-squares cycles reduced R to 0.047 and since the shifts in all parameters were less than 0.1 of an estimated standard deviation, the refinement was terminated.

All the calculations were carried out using an IBM 360 - Model 75 computer, with programs written or modified by GJP. The quantity minimized in the full matrix least-squares calculations was $\Sigma w(|F(obs)| - |F(calc)|)^2$ and the weighting scheme used was:

$$\sqrt{w} = |F(obs)|/2F(min) \quad \text{if } |F(obs)| < 2F(min)$$

$$\sqrt{w} = 1 \quad \text{if } 2F(min) < |F(obs)| < 6F(min)$$

$$\sqrt{w} = 6F(min)/F(obs) \quad \text{if } F(obs) > 6F(min)$$

where F(min), the nominal minimum F(obs), was 4.5. The scattering factors were taken from the usual source,[12] with the copper values corrected for the real part of the anomalous dispersion factor.[13]

The final positional and thermal parameters for the non-hydrogen atoms are tabulated in Table I, with the hydrogen parameters used in the calculations given in Table II. The observed and calculated structure amplitudes are given in Table III.

Discussion

A view of the structure projected onto (100) is shown in Figure 1 which also gives the atomic numbering. The Cu atom is located on a 2-fold axis of symmetry, while the DPPO ligand lies across a center of symmetry. The crystal consists of infinite chains of $CuCl_2$ units linked by the DPPO ligand. Therefore, the suggestion that the DPPO ligand acts as a bidentate chelate[10] is incorrect.

The geometry about the Cu atom is given in more detail in Figure 2 which illustrates the distorted nature of the adduct. The angle between the Cu–O–O′ and Cu–Cu–Cl′ planes is 57.7° (see Table IV), demonstrating the deviation from either a tetrahedral or square-planar geometry. A more regular configuration was found in both the $CuCl_2 \cdot 2DMSO$,[8] (DMSO is dimethyl sulfoxide) and $CuCl_2 \cdot 2LNO$,[3] (LNO is 2,6-lutinide-N-oxide) although both adducts show large distortions from an idealized geometry. Since the deviations from a tetrahedral structure for $CuCl_2 \cdot DPPO$ are somewhat smaller than from a square-planar geometry, we feel that the former is the preferred description.

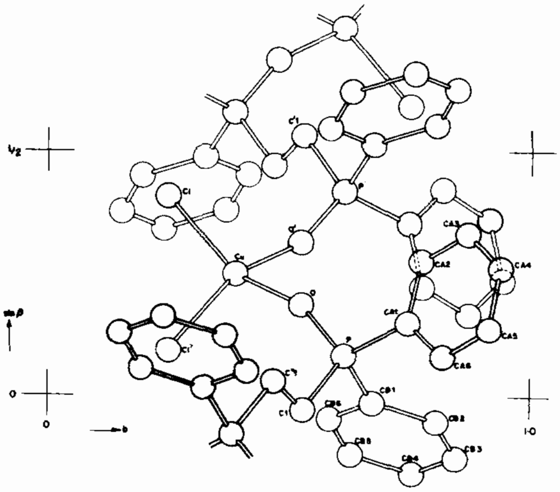

Figure 1. A view down the a axis illustrating the molecular packing and atomic numbering. The primed atoms are related to the unprimed atoms by a two-fold axis through the Cu atom. The atom C″1 is related to C1 by a center of symmetry midway between the C1-C″1 bond.

A comparison of the Cu–O distance of 1.959(3) Å found in $CuCl_2 \cdot DPPO$ with the distances in other $CuX_2 \cdot$ oxo-compound adducts reveals a remarkable fact. The Cu–O distances of 1.955(4) Å in $CuCl_2 \cdot$

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[12] *International Tables for X-ray Crystallography*, Vol. III, Kynoch Press, Birmingham, England (1962), P. 202.
[13] D. Cromer, *Acta Cryst.*, *18*, 17 (1965).

Table IV. The deviations (x 10^3) from the specified plane are given. The atoms used to specify the plane are in bold-face type.

Atom	Ring A	Ring B	$CuCl_2$ group	CuO_2 group	P—O—C1 **0**
C1	**2**	**7**			
C2	**1**	**—2**			
C3	**—5**	**—4**			
C4	**6**	**4**			
C5	**—3**	**1**			
C6	**—1**	**—6**			
P	113	—3		—744	**0**
O			1140	**0**[a]	**0**
Cl			**0**[a]		
Cu			**0**	**0**	—1004
			Parameters of the Planes[b]		
ℓ	0.6959	—0.5072	0.9902	0.4644	0.8031
m	—0.6815	0.2256	0.0	0.0	0.2597
n.	0.2263	0.8318	0.1400	0.8856	0.5362
p	—3.189	1.420	0.036	2.164	3.160

[a] The plane included the symmetry related atom. [b] The equation of the plane is, deviation = $\ell X + mY = nZ - p$, where X, Y, Z are the orthogonal coordinates in Å relative to a, b, c*.

2DMSO[8], 1.95(1) Å in $CuCl_2 \cdot 2LNO^3$ and 1.94 Å in $CuBr_2 \cdot 2PyNO^6$ (PyNO is pyridine-N-oxide) vary only slightly while the Cu–Cl distances vary from 2.195(1) Å in $CuCl_2 \cdot$ DPPO, to 2.221(4) and 2.247 (4) Å in $CuCl_2 \cdot 2LNO^3$ and 2.286(3) Å in $CuCl_2 \cdot$ 2DMSO.[8] A somewhat similar effect was noted in $ZnCl_2$ adducts with nitrogen bases. The Zn–N distances did not change appreciably but the Zn–Cl distances varied and were dependent on the nature of the oxo-molecule.[14] Unfortunately, the number of examples in both the $CuCl_2$ and $ZnCl_2$ cases is small and the accuracy of the determinations varied widely. Therefore, until additional studies are available, further speculation regarding these trends is premature.

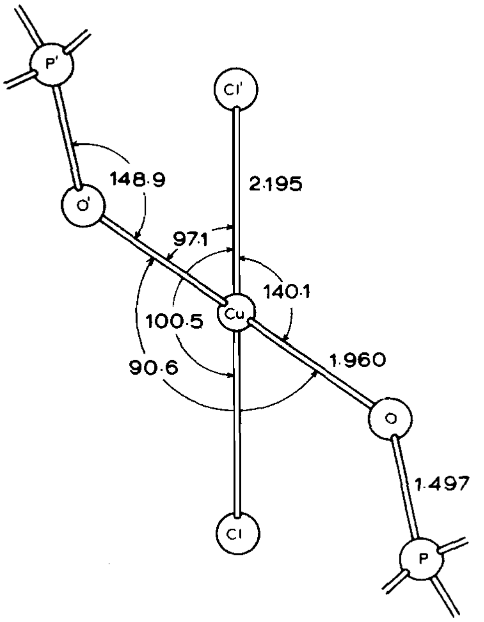

Figure 2. A view of the coordination sphere around the copper atom with the bond distances and angles involving the Cu and O atoms.

No other complexes of DPPO have been reported in the literature, so that a direct comparison of the dimensions involving the ligand is impossible. However, a comparison of the distances in the $CuCl_2 \cdot$ DPPO adduct with other phosphine and phosphine oxide complexes is informative. The P–C distances in triphenylphosphine oxide (avg. of 1.76(1) Å)[15] are shorter then in triphenylphosphine (avg. 1.828(5) Å),[16] a fact readily understood in terms of Bent's arguments involving s-character.[17] Furthermore, Bent's arguments predict that the P–C bonds in the DPPO ligand should be shorter than the P–C bonds in the DIPHOS ligand (DIPHOS is 1,2-bis(diphenylphosphine)ethane) complexes to either a Rh or Ni atom.[18,19] The shortening in DPPO results from a concentration of s-character in the P–C bonds when an O atom is bonded to the phosphorus relative to that in DIPHOS complexes where the O atom is replaced by a less electronegative Rh[18] or Ni[19] atom. The distances in $CuCl_2 \cdot$ DPPO of 1.809(3) Å from P to C(sp^3) and of 1.797(3) Å from P to C(sp^2) compared with 1.87(2) and 1.82(2) Å in the Rh complex[18] and 1.865(13) and 1.827(13) Å in the Ni complex[19] support this hypothesis. Similarly, the lengthening of the P–O bond from 1.46(1) Å in triphenylphosphine oxide[15] to 1.497 (2) Å in the $CuCl_2 \cdot$ DPPO complex can be rationalized on the basis of a change in s-character.

While the P–C–C–P chain is required to be planar by space group symmetry requirements, the usual conformation in DIPHOS complexes (where the ligand is chelating) is the symmetrical C_2 conformation.[18] However, since the DPPO ligand is bridging, the conformational requirements are expected to be different. The C–C distance of 1.522(8) Å is not significantly different from the value of 1.539(17) Å found in the Ni complex[19] nor from the value of 1.56(3) Å observed in the Rh complex.[18]

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(14) H.S. Preston and C.H.L. Kennard, *J. Chem. Soc.* (A), 1956 (1969).

(15) G. Bandoli, G. Bortolozzo, D.A. Clemente, U. Croatto, and C. Panattoni, *J. Chem. Soc.* (A), 2778 (1970).

(16) J.J. Daly, *J. Cehm. Soc.*, 3799 (1964).

(17) H.A. Bent, *Chem. Revs.*, *61*, 275 (1961).

(18) M.C. Hall, B.T. Kilbourn, and K.A. Taylor, *J. Chem. Soc.* (A), 2539 (1970).

(19) M.R. Churchill and T.A. O'Brien, *J. Chem. Soc.* (A), 206 (1970).

Table V. Bond lengths and angles in the bis(1,2-diphenylphosphinyl)ethane ligand with the estimated standard deviations in parentheses.

a. Bond lengths (Å)

P-CA1	=	1.793(3)	CA4-CA5	=	1.365(6)	CB1-CB2	=	1.382(5)
P-CB1	=	1.801(3)	CA5-CA6	=	1.378(5)	CB2-CB3	=	1.387(6)
CA1-CA2	=	1.390(5)	CA1-CA6	=	1.392(4)	CB3-CB4	=	1.376(6)
CA2-CA3	=	1.383(6)	P-C1	=	1.809(3)	CB4-CB5	=	1.369(6)
CA3-CA4	=	1.384(6)	C1-C1''	=	1.522(8)	CB5-CB6	=	1.395(5)
						CB6-CB1	=	1.378(5)

b. Angles (°)

O-P-C1	=	112.3(1)	CA2-CA3-CA4	=	120.2(4)	P-CB1-CB2	=	122.6(2)
O-P-CA1	=	108.8(1)	CA3-CA4-CA5	=	120.0(4)	P-CB1-CB6	=	117.5(2)
O-P-CB1	=	112.6(1)	CA4-CA5-CA6	=	120.5(3)	CB2-CB1-CB6	=	119.9(3)
CB5-CB6-CB1	=	119.9(3)	CA5-CA6-CA1	=	120.2(3)	CB1-CB2-CB3	=	119.9(3)
P-CA1-CA2	=	117.9(2)	P-C1-C1'	=	112.4(2)	CB2-CB3-CB4	=	120.1(4)
P-CA1-CA2	=	122.8(2)	C1-P-CA1	=	107.6(1)	CB3-CB4-CB5	=	120.3(4)
CA2-CA1-CA6	=	119.2(3)	C1-P-CB1	=	104.6(1)	CB4-CB5-CB6	=	119.9(4)
CA1-CA2-CA3	=	119.8(3)	CA1-P-CB	=	110.8(1)	CB5-CB6-CB1	=	119.9(3)

The C–C bond distances in the phenyl rings range from 1.365 to 1.395 Å with an average of 1.382(7) Å. Although this value is slightly smaller than the excepted value of 1.394 Å,[20] the absence of liberation corrections probably account for the small difference. The C–C–C angles average 120° as expected for planar hexagons (see Table IV); however, the P atom does not lie in the plane of ring A, (Figure 1). The large displacement of 0.113 Å of the P atom probably results from steric factors.

The van der Waals contacts appear to be normal with no intermolecular C–C distances of less than 3.80 Å. The only intermolecular contact less than 4.0 Å is CB5 to Cu of 3.94 Å.

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(20) *Chem. Soc. Special Publ.* No. 18, 1965, p. S16s.