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The Crystal Structure of Bis(triphenylphosphine)copper(I) Nitrate

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The crystal structure of bis(triphenylphosphine)copper(I) nitrate has been determined by a three-dimensional X-ray crystallographic analysis using diffractometer data. The colorless, acicular crystals are monoclinic (I2/a) with lattice parameters $a = 22.524 \pm 0.021$ Å, $b = 9.197 \pm 0.009$ Å, $c = 15.440 \pm 0.013$ Å, and $\beta = 101.56 \pm 0.07°$ and four molecules per unit cell. The structure was refined by least-squares methods using anisotropic thermal parameters to a final R of 0.074. All of the hydrogen atoms were located and included in the structure factor calculation but were not refined. The structure consists of $[(C_6H_5)_3P]_2CuNO_3$ molecules with symmetry C_2 separated by van der Waals distances. The copper atom is four-coordinate, the nitrate anion being bidentate. The important distances and angles are: Cu–P = 2.256 ± 0.003 Å, Cu–O = 2.223 ± 0.010 Å, Cu–N = 2.599 ± 0.025 Å, N–O = 1.257 ± 0.012 Å, P–Cu–P′ = $131.2 \pm 0.1°$, and O–Cu–O′ = $57.5 \pm 0.3°$.

Introduction

During a study of complexes of the type $L_4M^+X^-$, where L = triphenylphosphine $[(C_6H_5)_3P]$ or triphenylarsine $[(C_6H_5)_3As]$, M = Cu or Ag, and $X^- = ClO_4^-$, BrO_4^-, or NO_3^-, Cotton and Goodgame[1] reported the preparation of bis(triphenylphosphine)copper(I) nitrate. On the basis of conductivity and infrared evidence the authors suggested that the molecular structure of the complex was either a tricoordinate monomer or a nitrate-bridged dimer. The coordination mode of the nitrate ion could not be uniquely determined from the infrared spectra. Only 12 compounds containing coordinated nitrate ion have been the subject of crystal structure analyses,[2] and in all but one case, the nitrate is bidentate. Therefore, an X-ray structure analysis of $[(C_6H_5)_3P]_2CuNO_3$ was undertaken to determine the geometry of the compound and provide information on the coordination of the nitrate ion in Cu(I) compounds.

Experimental Section

Bis(triphenylphosphine)copper(I) nitrate was prepared by the method of Cotton and Goodgame.[1] Recrystallization by slowly cooling a hot, saturated ethanol solution provided clear, colorless, acicular crystals. Preliminary Weissenberg photographs taken with Cu Kα radiation indicated that the crystals were monoclinic. The systematic absences hkl when $h + k + l$ is odd and $h0l$ when h is odd indicate the space group to be Ia-C_s^4 or I2/a-C_{2h}^4 (nonstandard settings of Cc or C2/c). A second crystal with dimensions 0.07 × 0.07 × 0.21 mm³ was selected for intensity measurements. The crystal was mounted on a thin-glass fiber with the long axis of the crystal (the $\tilde{c}$ axis) parallel to the fiber axis and dipped in liquid nitrogen to minimize extinction effects. The crystal was aligned on a General Electric single-crystal orienter mounted on a General Electric XRD-6 diffractometer automated by the Datex Corp.

The unit cell parameters were determined from least-squares refinement of the 2θ settings for 24 reflections accurately centered on the orienter using a narrow beam (1° takeoff angle) of Zr-filtered Mo Kα ($\lambda(\alpha_1)$ 0.70926 Å, $\lambda(\alpha_2)$ 0.71354 Å) radiation. The α_1–α_2 doublet could be resolved for 2θ values greater than 25°. The cell parameter values are: $a = 22.524 \pm 0.021$ Å, $b = 9.197 \pm 0.009$ Å, $c = 15.440 \pm 0.013$ Å, and $\beta = 101.56 \pm 0.07°$. The experimental density of 1.40 g/cm³ determined by flotation in a carbon tetrachloride–*m*-xylene mixture agrees well with the density of 1.39 g/cm³ calculated on the basis of four molecules per unit cell. The intensity measurements were made with a scintillation counter using a wide beam of molybdenum radiation (nominal takeoff angle was 3°). A linear amplifier–pulse height selector combination and a 2-mil Zr filter were used to approximate monochromatic Mo Kα ($\lambda(\alpha)$ 0.7114 Å) radiation. Each reflection was counted for 20 sec, with the crystal and counter stationary. Four standard reflections were counted after every 100 reflections to monitor the crystal stability and alignment and beam stability. None of the four standard reflections showed any significant variation in intensity during the measurement of the first 2600 reflections to a 2θ of approximately 40°. However, during the measurement of the last 1268 reflections all four showed a steady decrease in intensity and the measurement of data was terminated when the standards had decayed to approximately 85% of their original values. The standard reflections were used to correct the data for this drop in intensity.

Reflections required to be absent by space group symmetry were measured and used to determine a background curve as a function of 2θ. Equivalent reflections were averaged and then the background correction was made. Of the 2001 independent reflections, 1343 reflections which were greater than or equal to 1.16 times the background were considered as observed reflections. The 658 unobserved reflections were entered as minus half the minimum observable counts (−0.08 times the background). The negative F is recognized by our computer programs as an unobserved reflection which may or may not be included in the calculation. Under the conditions of the intensity measurements, the α_1–α_2 doublet could be measured and no correction for the splitting was applied. These data were reduced to a set of observed amplitudes on an arbitrary scale following the application of Lorentz-polarization corrections. The linear absorption coefficient (μ) for this crystal with Mo Kα radiation is 8.78 cm^{-1}. No absorption corrections were made on the data since the upper limit to the variation of intensity due to absorption is estimated to be 13% with transmission coefficients ranging from 0.94 to 0.82. It has been shown[3] that atomic positions are not significantly affected by absorption corrections but our estimates of error of thermal parameters may be somewhat optimistic.

Solution and Refinement of the Structure

A statistical analysis of the distribution of intensities[4] indicated that the probable space group was C_{2h}^6-I2/a; the structure was solved and refined on this basis. In

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[1] F. A. Cotton and D. M. L. Goodgame, *J. Chem. Soc.*, 5267 (1960).

[2] K. J. Coskran, T. J. Huttemann, and J. G. Verkade, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1966, p 590.

[3] R. C. Srivastava and E. C. Lingafelter, *Acta Cryst.*, **20**, 918 (1966).

[4] E. R. Howells, D. C. Phillips, and D. Rogers, *ibid.*, **3**, 210 (1950).

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES FOR $[(C_6H_5)_3P]_2CuNO_3$[a]

L	FO	FC
H= 0, K= 0		
2	2145	2168
4	473	415
6	833	828
8	146	64
10	-84	-55
12	138	-187
14	-53	49
16	-87	65
H= 2, K= 0		
-16	261	-216
-12	234	-214
-10	888	-814
-8	904	-875
-6	654	-703
-4	3325	-3485
-2	2110	-2034
0	1807	-1778
2	450	-499
4	1273	-1365
6	-92	-225
8	204	-200
10	419	-436
12	160	-178
14	384	-382
H= 4, K= 0		
-16	232	193
-14	-92	166
-12	1036	1057
-10	1046	972
-8	1577	1601
-6	1224	1238
-4	373	402
-2	1293	1241
0	447	-348
2	479	732
4	461	453
6	581	551
8	420	394
10	341	341
12	471	457
14	723	705
H= 6, K= 0		
-16	354	-344
-14	567	-525
-12	871	-825
-10	274	-257
-8	420	-394
-6	129	-226
-4	803	-816
-2	2509	-2605
0	1118	1048
2	2820	-2828
4	1302	-1306
6	214	-223
8	-83	-121
10	707	-656
12	683	-669
14	282	-319
H= 8, K= 0		
-16	241	226
-12	436	408
-10	-79	-54
-8	236	-209
-6	844	898
-4	823	873
-2	1000	947
0	557	473
2	2248	2308
4	635	694
6	1188	1141
8	746	703
10	386	424
12	230	306
14	-87	-104
H= 10, K= 0		
-16	127	-122
-14	330	-333
-12	269	242
-10	-78	-99
-8	183	-142
-6	142	-173
-4	469	-503
-2	1536	-1580
0	2190	-2273
2	1497	-1620
4	735	-710
6	656	-628
10	137	-109
12	-93	46
H= 12, K= 0		
-14	131	102
-12	-81	38
-10	441	404
-8	182	213
-6	616	609
-4	485	451
-2	883	505
0	2408	2350
2	277	272
4	691	660
6	301	319
8	-81	96
10	143	52
12	-81	61
H= 14, K= 0		
-14	145	-67
-12	492	-460
-10	993	-572
-8	538	-561
-6	563	-493
-4	1392	-1280
-2	738	-722
0	1040	-816
2	218	184
4	-78	-125
6	222	186
8	-81	-63
H= 16, K= 0		
-14	249	188
-12	344	328
-10	267	260
-8	692	672
-6	457	483
-4	539	521
-2	437	434
0	637	153
2	-77	81
4	254	251
6	-81	33
8	133	99
10	254	211
H= 18, K= 0		
-12	466	-468
-10	-80	47
-8	-79	0
-6	118	111
-4	-79	-28
-2	-79	58
0	492	284
4	654	-686
6	224	-214
H= 20, K= 0		
-10	258	-198
-8	-73	43
-6	245	145
-4	159	-133
0	673	585
2	499	487
4	-74	73
6	385	342
H= 22, K= 0		
-8	-75	-108
-6	274	-312
-4	477	-500
-2	416	-430
0	314	-249
2	262	-237
H= 24, K= 0		
-4	-77	134
-2	246	227
H= 0, K= , 1		
1	547	551
3	1610	1582
5	668	604
7	-90	-147
9	134	116
11	-85	93
13	609	587
15	-92	112
H= 1, K= 1		
-16	-87	25
-14	-93	-97
-12	246	254
-10	-84	-99
-8	537	-551
-6	419	-460
-4	318	-365
-2	1836	-1764
0	2123	-2038
2	991	-1033
4	1138	-1136
6	139	-206
8	-87	-88
10	-84	36
12	-88	130
14	-94	-9
16	144	63
H= 2, K= 1		
-13	401	-404
-11	-85	20
-9	253	-224
-7	510	-466
-5	954	-942
-3	3159	-3126
-1	300	-329
1	-109	-115
3	-110	-118
5	313	-361
7	530	518
9	495	-497
11	320	-325
13	-91	-82
15	-90	-120
H= 3, K= 1		
-16	-88	72
-14	-92	51
-12	269	238
-10	950	892
-8	780	769
-6	1211	1173
-4	1486	1463
-2	-112	229
0	675	-667
2	582	-641
4	178	-242
6	-91	-24
8	192	176
10	123	148
12	330	320
14	246	209
H= 4, K= 1		
-15	-93	177
-13	308	321
-11	161	160
-9	163	-187
-7	591	421
-5	-86	56
-3	1074	-1088
-1	392	428
1	3872	3809
3	190	-209
5	864	849
7	510	515
9	-86	159
11	163	224
13	-93	-113
15	-88	94
H= 5, K= 1		
-16	-88	-161
-14	201	-242
-12	622	-408
-10	770	-738
-8	1029	-1024
-6	1350	-1306
-4	-97	132
-2	594	559
0	570	510
2	465	533
4	196	183
6	275	-290
8	288	-296
10	339	-329
12	519	-535
14	322	-290
H= 6, K= 1		
-15	195	-204
-13	-90	37
-11	450	-447
-9	226	-208
-7	360	335
-5	597	538
-3	1647	-1614
-1	1645	-1662
1	1590	-1586
3	-84	-213
5	-84	-110
7	476	-443
9	-85	-123
11	-89	-161
13	-94	-39
H= 7, K= 1		
-16	325	305
-14	226	249
-12	581	401
-10	334	332
-8	-82	-55
-6	323	-302
-4	-84	-82
-2	-83	44
0	342	-327
2	572	609
4	753	745
6	549	575
8	512	462
10	521	484
12	316	351
14	-88	48
H= 8, K= 1		
-15	-93	128
-13	-90	-80
-11	425	461
-9	252	203
-7	620	590
-5	243	297
-3	202	256
-1	2067	2058
1	417	466
3	-84	219
5	-83	-129
7	290	286
9	-86	111
11	-91	186
13	-92	140
H= 9, K= 1		
-16	-87	-101
-14	-94	-121
-12	122	-110
-10	431	429
-8	-80	16
-6	429	-448
-4	457	-456
-2	393	-450
0	588	-573
2	706	-706
4	619	-599
6	744	-720
8	598	-596
10	273	-279
12	-94	107
H= 10, K= 1		
-15	-91	-147
-13	248	-215
-11	477	-477
-9	247	-271
-7	-81	120
-5	646	-614
-3	447	-484
-1	134	-200
1	441	406
3	1169	-1190
5	185	-206
7	-78	-8
9	-81	-36
11	-93	-162
13	157	-247
H= 11, K= 1		
-14	-80	-25
-12	219	-223
-10	144	129
-8	448	440
-6	-82	129
-4	463	472
-2	721	704
0	940	973
2	772	766
4	604	590
6	413	441
8	-80	81
10	-81	-82
12	-90	-112
H= 12, K= 1		
-15	-81	90
-13	234	237
-11	123	-20
-9	183	207
-7	-80	62
-5	414	447
-3	407	389
-1	463	504
1	297	275
3	728	668
5	-79	204
7	-80	54
11	-80	73
H= 13, K= 1		
-14	175	-143
-12	140	-176
-10	521	-526
-8	548	-525
-6	568	-542
-4	807	-754
-2	625	-574
0	373	-375
2	154	-149
4	-79	32
6	193	213
8	-81	53
10	-80	-67
H= 14, K= 1		
-15	-81	-133
-13	336	-345
-11	236	271
-9	-80	16
-7	121	-78
-5	248	-250
-3	436	-423
-1	388	-311
1	705	-747
3	531	-560
5	-79	-122
7	-81	46
9	174	-201
11	-81	-33
H= 15, K= 1		
-14	-81	139
-12	169	169
-10	589	601
-8	679	650
-6	787	762
-4	497	471
-2	175	219
0	-74	14
2	423	-388
4	149	-206
6	-81	28
8	-80	96
10	-81	78
H= 16, K= 1		
-13	180	244
-11	-80	122
-9	-81	101
-7	252	294
-5	-76	127
-3	-75	110
-1	333	382
1	330	353
3	403	-401
5	300	325
9	-81	109
H= 17, K= 1		
-12	284	-296
-10	228	-255
-8	-80	-82
-6	156	-127
-4	-77	29
-2	-77	167
0	-78	107
2	220	-206
4	353	-368
6	-80	-173
8	184	-132
H= 18, K= 1		
-13	-81	51
-11	290	-298
-9	329	-311
-7	-80	-43
-5	-80	-6
-3	288	-294
-1	-79	-153
1	299	-341
3	-76	53
5	-80	-78
7	-81	-114
H= 19, K= 1		
-12	248	222
-10	141	-30
-8	-76	-83
-6	-79	-27
-4	-80	-71
-2	-80	-31
0	176	160
2	352	341
4	272	241
6	262	267
H= 20, K= 1		
-11	-81	135
-9	121	-86
-7	-74	25
-5	-77	32
-3	269	283
-1	282	372
1	155	224
3	140	135
5	-75	49
H= 21, K= 1		
-10	186	115
-8	176	-144
-6	-72	-104
-4	187	-178
-2	281	-310
0	220	-229
2	161	-210
4	185	-167
H= 22, K= 1		
-9	-77	-79
-7	-75	-41
-5	143	-123
-3	140	-226
-1	-74	-37
1	-75	114
3	131	-231
H= 23, K= 1		
-8	154	156
-6	228	203
-4	262	320
-2	283	246
0	201	218
H= 24, K= 1		
-3	-77	-172
H= 0, K= 2		
0	1409	1305
2	1309	-1370
4	1671	-1677
6	695	-634
8	-85	-27
10	-86	34
12	152	151
14	-94	8
H= 1, K= 2		
-15	-91	-85
-13	366	-369
-11	491	-485
-9	385	-362
-7	853	-818
-5	1156	-1138
-3	518	-581
-1	260	-274
1	505	494
3	331	399
5	722	-737
7	442	-451
9	404	-394
11	573	-569
13	218	-181
15	165	-159
H= 2, K= 2		
-16	-93	-1
-12	-88	-23
-10	168	182
-8	390	434
-6	1470	1580
-4	181	212
-2	1910	1952
0	838	830
2	286	-311
4	875	823
6	-90	85
8	-83	18
10	-85	-41
12	-89	-104
14	-94	-90
H= 3, K= 2		
-15	-92	-35
-13	171	159
-11	-86	107
-9	202	212
-7	336	340
-5	1248	1170
-3	1720	1676
-1	588	567
1	1108	1018
3	455	638
5	286	336
7	589	550
9	471	457
11	-88	46
13	-93	-109
15	157	149
H= 4, K= 2		
-16	126	30
-14	-93	-134
-12	226	-224
-10	553	-561
-8	587	-588
-6	1788	-1769
-4	728	-808
-2	-90	-140
0	149	-193
2	244	255
4	-84	40
6	363	401
8	414	-367
10	184	-194
12	189	-218
14	-92	-71
H= 5, K= 2		
-15	-92	-16
-13	362	-350
-11	-86	-26
-9	540	-496
-7	981	-991
-5	-84	-127
-3	-81	49
-1	344	-325
1	398	-375
3	972	-929
5	911	-875
7	695	-637
9	517	-482
11	-89	-41
13	-94	14
H= 6, K= 2		
-16	145	133
-14	152	221
-12	352	368
-10	710	673
-8	782	759
-6	-84	60
-4	481	-434
-2	292	-299
0	147	171
2	958	-860
4	218	-153
6	666	668
8	896	854
10	258	268
12	945	371
14	137	170
H= 7, K= 2		
-15	-92	184
-13	-91	62
-11	402	386
-9	854	790
-7	-83	80
-5	-84	102
-3	896	860
-1	913	886
1	686	659
3	-84	195
5	225	283
7	448	419
9	255	297
11	191	219
13	247	241
H= 8, K= 2		
-16	174	-175
-14	-94	-41
-12	-81	-146
-10	-78	-80
-8	-80	-60
-6	843	821
-4	-70	-104
-2	386	328
0	-73	-79
2	862	-778
4	782	-805
6	660	-674
8	680	-671
10	397	-380
12	-94	-47
H= 9, K= 2		
-15	251	-234
-13	144	-96
-11	229	-223
-9	302	-311
-7	811	-814
-5	817	-827
-3	423	-439
-1	-70	-155
1	-66	-145
3	210	-287
5	162	-195
7	345	-331
9	321	-325
11	-93	-219
13	127	-160
H= 10, K= 2		
-14	182	-146
-12	116	-171
-10	383	-409
-8	-80	38
-6	204	241
-4	781	752
-2	242	229
0	859	860
2	871	857
4	701	704
6	765	736
8	-80	-68
10	-81	-47
12	-91	-78
H= 11, K= 2		
-15	-81	70
-13	-80	-37
-11	600	581
-9	623	631
-7	616	617
-5	530	523
-3	137	179
-1	-69	8
1	-69	-29
3	414	387
5	587	566
7	275	262
9	-81	-25
11	116	126
H= 12, K= 2		
-14	159	154
-12	-81	105
-10	203	-196
-8	418	-453
-6	476	-461
-4	1157	-1111
-2	761	-712
0	-70	25
2	498	-507
4	224	-242
6	-79	65
8	220	234
10	-80	7
12	-81	75
H= 13, K= 2		
-15	-81	-38
-13	194	-214
-11	193	-209
-9	124	124
-7	289	-302
-5	575	-561
-3	479	-439
-1	560	-596
1	580	-559
3	454	-474
5	-79	-163
7	-81	-41
9	129	-180
11	140	-152
H= 14, K= 2		
-14	188	149
-12	166	146
-10	127	128
-8	583	548
-6	1049	1000
-4	106	43
-2	164	140
0	-73	22
2	142	-112
4	-79	-152
6	-81	-94
8	-80	29
10	-81	79
H= 15, K= 2		
-13	208	224
-11	-81	15
-9	-81	122
-7	174	208
-5	344	344
-3	207	223
-1	-74	132
1	217	236
3	145	182
5	324	322
7	409	435
9	198	212
H= 16, K= 2		
-12	290	-211
-10	354	-385
-8	-80	-96
-6	281	-252
-4	-76	88
-2	-76	-95
0	141	224
2	224	267
4	-80	-78
6	165	-137
8	144	-180
H= 17, K= 2		
-13	210	-188
-11	130	-129
-9	494	-515
-7	319	-346
-5	-79	-97
-3	218	-245
-1	-78	-162
1	-79	-28
3	124	-152
5	-80	-196
7	121	-123
H= 18, K= 2		
-12	-81	91
-10	232	208
-8	-77	-18
-6	-80	-30
-4	134	-193
-2	-80	-60
0	-81	158
2	-79	13
4	-75	22
6	221	204
H= .19, K= 2		
-11	-81	83
-9	299	282
-7	206	218
-5	245	290
-3	236	267
-1	292	355
3	-74	-14
5	-80	-12
H= 20, K= 2		
-10	-75	31
-8	-73	63
-6	139	180
-4	-76	-141
-2	-76	-41
0	-75	-45
2	289	-249
4	270	-274
H= 21, K= 2		
-7	-74	-86
-5	-73	-102
-3	187	-163
-1	139	-132
1	-74	-46
3	127	-145
H= 22, K= 2		
-8	-74	74
-6	-75	21
-4	208	201
-2	221	194
0	224	234
2	151	159
H= 23, K= 2		
-7	133	114
-5	-76	170
-3	-76	51
-1	-76	-4
H= 0, K= 3		
1	730	-722
3	307	-49
5	-84	-179
7	1068	-1047
9	665	-623
11	681	-627
13	336	-355
15	129	-140
H= 1, K= 3		
-14	347	-313
-12	-90	-98
-10	-85	-23
-8	365	-340
-6	-84	208
-4	1217	1216
-2	786	824
0	736	679
2	670	-594
4	624	-542
6	323	-310
8	638	-409
10	625	-628
12	-90	-138
14	-93	5
H= 2, K= 3		
-15	172	161
-13	-92	135
-11	224	241
-9	555	540
-7	395	433
-5	1085	1156
-3	1579	1590
-1	-82	109
1	1218	1178
3	785	789
5	458	498
7	1078	1032
9	266	278
11	404	426
13	149	203
15	-86	18
H= 3, K= 3		
-14	-94	32
-12	-89	-163
-10	-85	-38
-8	-80	-112
-6	466	-446
-4	247	-366
-2	511	-550
0	218	-82
2	-75	89
4	654	638
6	1265	1193
8	369	369
10	210	207
12	194	199
14	-91	-104
H= 4, K= 3		
-15	-90	-44
-13	-92	-89
-11	-87	-99
-9	583	-575
-7	304	-340
-5	1041	-1114
-3	1091	-1068
-1	470	-499
1	1597	-1580
3	1334	-1428
5	962	-956
7	672	-680
9	268	-261
11	-89	19
13	-94	-14
H= 5, K= 3		
-14	170	249
-12	231	276
-10	234	246
-8	135	-168
-6	511	-481
-4	542	-478
-2	-74	79
0	584	-552
2	786	-718
4	618	-547
6	236	-233
8	-79	114
10	-88	95
12	-93	127
14	189	184
H= 6, K= 3		
-15	169	201
-13	-92	190
-11	231	178
-9	745	656
-7	749	768
-5	903	944
-3	258	291
-1	929	989
1	653	731
3	391	459
5	987	955
7	242	295
9	343	341
11	214	289
13	143	175
H= 7, K= 3		
-14	-94	-223
-12	-81	0
-10	114	72
-8	-80	90
-6	556	534
-4	1018	1006
-2	451	433
0	448	424
2	211	226
4	-83	77
6	191	-201
8	243	-260
10	303	-300
12	-94	-117
H= 8, K= 3		
-15	177	-207
-13	242	-244
-11	395	-393
-9	250	-276
-7	355	-379
-5	1053	-1033
-3	662	-708
-1	492	-533
1	-67	-106
3	630	-611
5	694	-704
7	261	-281
9	513	-543
11	235	-227
13	-88	-106
H= 9, K= 3		
-14	-80	17
-12	240	-234
-10	138	-147
-8	429	-435
-6	898	-866
-4	542	-515
-2	288	-339
0	589	508
2	970	895
4	237	267
6	264	220
8	-80	-104
10	-81	-86
12	146	46
H= 10, K= 3		
-15	-81	107
-13	198	171
-11	236	241
-9	457	451
-7	1030	1023
-5	296	298
-3	411	429
-1	909	902
1	288	290
3	297	328
5	390	423
7	462	455
9	259	257
11	-80	24
H= 11, K= 3		
-14	-80	132
-12	191	167
-10	440	428
-8	282	259
-6	-73	-41
-4	456	-412
-2	642	-594
0	451	-446
2	-72	-149
4	-79	-107
6	209	224
8	342	370
10	122	113
12	-81	78
H= 12, K= 3		
-13	132	-123
-11	466	-473
-9	397	-388
-7	678	-626
-5	522	-500
-3	764	-781
-1	337	-340
1	253	-270
3	554	-549
5	216	-208
7	203	-208
9	163	-171
11	208	-206
H= 13, K= 3		
-14	191	-250
-12	-80	-75
-10	-81	-12
-8	-79	40
-6	478	416
-4	599	539
-2	-73	107
0	274	250
2	-75	-78
4	234	-245
6	211	-226
8	209	-218
10	154	-226
H= 14, K= 3		
-13	164	250
-11	210	224
-9	-81	91
-7	-78	101
-5	258	241
-3	405	397
-1	285	291
1	729	681
3	337	364
5	248	282
7	453	506
9	125	159
H= 15, K= 3		
-12	283	-264
-10	-81	-43
-8	-80	-2
-6	-78	-13
-4	-76	89
-2	-76	154
0	205	234
2	-78	186
4	-81	111
6	190	221
8	-80	36
H= 16, K= 3		
-13	-81	-52
-11	-80	0
-9	363	-365
-7	222	-225
-5	287	-300
-3	413	-341
-1	-78	-141
1	342	-396
3	387	-376
5	301	-293
7	204	-226
H= 17, K= 3		
-12	-81	135
-10	180	197
-8	-77	1
-6	245	-271
-4	208	-264
-2	-80	-115
0	283	-322
2	271	-335
4	166	-197
6	-80	45
8	166	191
H= 18, K= 3		
-11	131	120
-9	332	334
-7	451	437
-5	509	525
-3	231	232
-1	212	242
1	169	162
3	145	141
5	145	171
7	-81	-5
H= 19, K= 3		
-10	164	172
-8	156	137
-6	-75	207
-4	261	314
-2	-77	0
0	-76	-83
2	146	-121
4	181	-120
6	-81	-70
H= . 20, K= 3		
-9	167	-194
-7	177	-188
-5	235	-197
-3	191	-124
-1	346	-371
1	-73	-140
3	-75	-61
5	110	-151
H= 21, K= 3		
-8	215	-241
-6	145	-177
-4	-74	51
-2	124	135
0	210	199
2	187	191
H= 22, K= 3		
-7	152	116
-5	149	169
-3	185	138
-1	-76	107
1	-77	41
H= 23, K= 3		
-4	-77	-99
-2	-77	-47
H= 0, K= 4		
0	561	-510
2	134	-26
4	284	-284
6	-81	-145
8	338	-318
10	424	-391
12	303	-294
14	330	-318
H= 1, K= 4		
-15	269	199
-13	-94	192
-11	142	159
-9	296	310
-7	330	326
-5	308	-288
-3	741	753
-1	800	830
1	602	663
3	627	619
5	-83	130
7	162	181
9	244	241
11	428	432
13	178	260
H= 2, K= 4		
-14	262	265
-12	258	223
-10	-79	-41
-8	-79	-30
-6	169	-171
-4	557	-553
-2	-70	60
0	124	139
2	176	-117
4	1247	1243
6	1232	1145
8	984	925
10	720	683
12	-93	96
14	-88	29
H= 3, K= 4		
-15	136	-116
-13	151	-232
-11	155	-105
-9	-78	3
-7	443	-452
-5	272	-308
-3	228	-258
-1	369	-402
1	897	-882
3	937	-962
5	692	-675
7	-79	49
9	219	-225
11	337	-394
13	-92	-50
H= 4, K= 4		
-14	-91	81
-12	-81	-52
-10	-79	67
-8	155	-123
-6	530	-492
-4	195	-177
-2	457	-458
0	660	-635
2	822	-793
4	986	-490
6	626	-626
8	345	-276
10	-81	-162
12	-94	-4
14	-86	14
H= 5, K= 4		
-15	136	174
-13	-80	27
-11	-81	45
-9	276	300
-7	-80	163
-5	200	229
-3	248	250
-1	952	1019
1	1505	1470
3	244	278
5	332	359
7	258	243
9	-60	32
11	-81	16
13	-90	169
H= 6, K= 4		
-14	149	-81
-12	-81	67
-10	157	130
-8	346	342
-6	338	364
-4	1071	1006
-2	1397	1374
0	453	694
2	937	914
4	-81	100
6	-79	-1
8	-79	-95
10	156	-180
12	-80	59
H= 7, K= 4		
-15	-85	-144
-13	152	-182
-11	-81	-115
-9	113	-122
-7	133	-131
-5	757	-700
-3	739	-717
-1	631	-667
1	307	-336
3	425	-549
5	349	-350
7	-78	46
9	179	-195
11	-80	-85
H= 8, K= 4		
-14	-81	-48
-12	227	-170
-10	336	-340
-8	575	-511
-6	736	-702
-4	784	-848
-2	474	-471
0	106	-113
2	442	-385
4	-80	115
6	-78	-4
8	-81	-103
10	-80	-55
12	-81	-53
H= 9, K= 4		
-13	200	211
-11	366	413
-9	218	217
-7	-78	23
-5	541	514
-3	499	477
-1	682	671
1	227	237
3	-73	82
5	126	153
7	323	315
9	-81	84
H= 10, K= 4		
-14	234	205
-12	151	115
-10	343	337
-8	433	434
-6	578	557
-4	540	492
-2	-72	-9
0	-72	105
2	-73	142
4	-75	11
6	121	207
8	121	143
10	-80	103
H= 11, K= 4		
-13	257	-231
-11	201	-201
-9	189	-189
-7	234	-232
-5	203	-170
-3	386	-339
-1	422	-450
1	269	-256
3	364	-310
5	118	-74
7	160	-163
9	154	-138
11	160	-168
H= 12, K= 4		
-14	298	-270
-12	266	-225
-10	416	-431
-8	296	-239
-6	-76	0
-4	223	192
-2	248	230
0	110	-62
2	-75	17
4	334	-313
6	297	-346
8	286	-321
10	286	-285
H= 13, K= 4		
-13	172	164
-11	185	209
-9	-81	116
-7	-79	26
-5	-76	27
-3	413	369
-1	219	186
1	417	384
3	447	426
5	123	132
7	117	175
9	-80	114
H= 14, K= 4		
-12	144	125
-10	-80	30
-8	-80	93
-6	-79	10
-4	174	-161
-2	118	141
0	218	259
2	-79	139
4	415	470
6	328	291
8	255	260
H= 15, K= 4		
-13	126	-136
-11	-80	34
-9	152	-72
-7	363	-315
-5	-79	74
-3	201	-168
-1	536	-496
1	498	-476
3	239	-179
5	-80	-139
7	-80	-53
H= 16, K= 4		
-12	117	115
-10	169	204
-8	-76	82
-6	271	-295
-4	542	-502
-2	660	-685
0	461	-519
2	258	-315
4	299	-353
6	-80	-134
8	124	27
H= 17, K= 4		
-11	-81	103
-9	140	136
-7	123	125
-5	298	311
-3	255	216
-1	121	118
1	320	320
3	180	162
5	164	162
7	-81	28
H= 18, K= 4		
-10	128	144
-8	230	227
-6	243	263
-4	358	370
-2	231	268
0	134	190
2	273	296
4	-74	87
6	-81	20
H= 19, K= 4		
-9	149	-93
-7	143	-85
-5	249	-219
-3	180	-168
-1	179	-158
1	160	-144
3	149	-95
5	-77	-64
H= 20, K= 4		
-8	229	-253
-6	210	-225
-4	-74	-186
-2	-76	24
0	-74	56
2	-76	-54
H= 21, K= 4		
-7	-77	46
-5	164	144
-3	183	164
-1	-76	156
1	-77	0
H= 22, K= 4		
-4	-77	40
-2	-77	20
H= 0, K= 5		
1	-65	29
3	262	261
5	-80	-54
7	273	293
9	-80	1
11	-81	-22
13	-80	-28
H= 1, K= 5		
-14	321	309
-12	335	291
-10	408	362
-8	-79	-47
-6	288	-337
-4	237	185
-2	533	523
0	893	826
2	158	142
4	340	327
6	986	924
8	745	743
10	175	176
12	357	335
H= 2, K= 5		
-13	-80	-46
-11	180	-171
-9	-80	-85
-7	-76	-61
-5	458	433
-3	429	415
-1	315	-308
1	233	144
3	252	-241
5	147	-261
7	160	-158
9	-81	-110
11	226	-205
13	-81	5
H= 3, K= 5		
-14	147	-180
-12	181	-148
-10	178	-172
-8	144	169
-6	136	164
-4	324	-339
-2	396	-409
0	357	-409
2	829	-806
4	843	-840
6	763	-757
8	831	-816
10	303	-292
12	-80	-81
H= 4, K= 5		
-13	-80	105
-11	-81	16
-9	-80	2
-7	-78	-35
-5	164	193
-3	-71	-79
-1	-70	64
1	301	-252
3	125	70
5	-79	41
7	127	99
9	181	182
11	154	163
H= 5, K= 5		
-14	-81	1
-12	168	139
-10	154	155
-8	-79	-70
-6	147	160
-4	441	434
-2	1282	1229
0	939	937
2	902	872
4	793	732
6	324	377
8	114	-31
10	163	-25
12	-81	105
H= 6, K= 5		
-13	-80	11
-11	-81	100
-9	135	-128
-7	-78	95
-5	282	-268
-3	-72	-143
-1	366	-304
1	249	-223
3	149	-168
5	251	-244
7	-80	20
9	-81	86
11	-80	97
H= 7, K= 5		
-14	-81	-24
-12	132	-199
-10	158	-178
-8	225	-258
-6	623	-610
-4	749	-745
-2	1131	-1123
0	1108	-1050
2	781	-751
4	165	-196
6	-79	143
8	231	262
10	156	-140
12	-81	-66
H= 8, K= 5		
-13	-81	65
-11	-80	78
-9	139	177
-7	-79	55
-5	373	399
-3	349	353
-1	-73	-23
1	215	191
3	-74	12
5	155	-124
7	153	-195
9	-80	40
11	-81	-68
H= 9, K= 5		
-12	174	154
-10	259	232
-8	665	665
-6	730	781
-4	541	519
-2	365	315
0	459	425
2	445	413
4	-77	-164
6	-81	-107
8	-81	55
10	210	204
H= 10, K= 5		
-13	117	-90
-11	126	-127
-9	-81	-112
-7	260	-254
-5	177	-96
-3	112	111
-1	126	134
1	-75	-66
3	260	264
5	-81	-1
7	132	-96
9	138	-160
H= 11, K= 5		
-12	290	-292
-10	209	-258
-8	436	-452
-6	153	-124
-4	-76	121
-2	-75	-43
0	123	-159
2	129	-107
4	262	-285
6	198	-261
8	220	-244
10	272	-224
H= 12, K= 5		
-13	-81	42
-11	155	109
-9	-81	17
-7	-80	-82
-5	365	-385
-3	-77	6
-1	-77	-62
1	-78	47
3	167	121
5	141	119
7	152	153
H= 13, K= 5		
-12	221	237
-10	280	279
-8	-74	-51
-6	231	-210
-4	-79	-42
-2	-78	68
0	345	362
2	274	270
4	316	313
6	360	367
8	339	314
H= 14, K= 5		
-11	-81	-27
-9	-73	25
-7	276	-276
-5	-80	1
-3	-80	-19
-1	126	-110
1	-80	19
3	-78	2
5	-74	18
7	-80	-82
H= 15, K= 5		
-10	-80	59
-8	161	161
-6	133	-145
-4	541	-536
-2	407	-457
0	338	-330
2	281	-303
4	328	-318
6	235	-202
H= 16, K= 5		
-11	-81	47
-9	-74	66
-7	-73	14
-5	-76	58
-3	212	176
-1	143	157
1	-76	-16
3	131	150
5	146	77
H= 17, K= 5		
-10	130	97
-8	-74	38
-6	103	127
-4	438	434
0	355	326
2	358	293
4	320	265
H= 18, K= 5		
-9	-76	66
-7	-74	125
-5	191	-163
-3	-73	-6
-1	174	-58
1	178	-135
3	183	-79
H= 19, K= 5		
-8	249	-242
-6	250	-324
-4	-74	-89
-2	-74	-150
0	260	-242
2	150	-189
H= 20, K= 5		
-5	187	157
-3	-76	12
-1	-76	-78
1	-77	-64
H= 0, K= 6		
0	134	-156
2	-73	51
4	112	135
6	437	456
8	267	247
10	421	383
12	308	274
H= 1, K= 6		
-11	-80	66
-9	-81	-8
-7	191	122
-5	243	263
-3	276	239
-1	255	256
1	-73	72
3	197	157
5	155	-197
7	567	-557
9	129	79
H= 2, K= 6		
-12	215	-153
-10	355	-346
-8	123	79
-6	180	-177
-4	112	87
-2	-73	-163
0	-73	-113
2	185	-227
4	480	-485
6	562	-562
8	920	-521
10	271	-291
12	294	-264
H= 3, K= 6		
-13	-81	-52
-9	137	161
-7	461	-435
-5	338	-352
-3	-74	-55
-1	327	-356
1	233	-240
3	-74	-87
5	-77	122
7	401	430
9	126	62
11	-80	-18
H= 4, K= 6		
-12	-80	29
-10	-81	61
-8	-81	-100
-6	182	178
-4	114	147
-2	343	379
0	288	308
2	583	557
4	711	736
6	348	364
8	447	436
10	-80	87
12	-81	44
H= 5, K= 6		
-13	-81	25
-11	-80	65
-9	197	203
-7	183	217
-5	269	-287
-3	341	-349
-1	-74	-1
1	263	268
3	-75	57
5	-78	-89
7	142	171
9	-80	88
11	-81	-40
H= 6, K= 6		
-10	-80	-105
-8	334	-347
-6	293	-328
-4	339	-364
-2	699	-674
0	968	-907
2	445	-457
4	441	-431
6	151	-77
8	-81	-95
10	-80	85
H= 7, K= 6		
-13	173	-160
-11	-80	-6
-9	-81	22
-7	159	151
-5	261	287
-3	-76	-65
-1	-75	-23
1	-76	-103
3	-77	-41
5	-80	39
7	246	-229
9	-80	-86
11	-81	-23
H= 8, K= 6		
-12	114	155
-10	216	234
-8	540	593
-6	459	443
-4	981	926
-2	561	530
0	317	343
2	-77	124
4	-79	-63
6	155	-159
8	-80	-38
10	140	104
H= 9, K= 6		
-11	-80	94
-9	-81	-30
-7	304	-354
-5	-79	-47
-3	466	421
-1	178	194
1	-78	-121
3	-79	-84
5	201	224
7	190	201
9	-81	-86
H= 10, K= 6		
-12	254	-302
-10	250	-278
-8	629	-646
-6	399	-382
-4	211	-215
-2	137	189
0	-78	41
2	-79	108
4	-80	79
6	280	-290
8	-80	-123
H= 11, K= 6		
-11	-81	-105
-9	-80	-20
-7	-78	40
-5	265	-281
-3	-80	-80
-1	-79	17
1	170	-191
3	-79	-171
5	-76	-30
7	-80	87
9	-81	77
H= 12, K= 6		
-10	183	273
-8	146	62
-6	147	-89
-4	-80	18
-2	-81	-35
0	-80	-63
2	217	222
4	276	290
6	320	303
8	122	112
H= 13, K= 6		
-11	-81	-21
-9	124	-62
-7	-75	-30
-5	-78	149
-3	218	231
-1	244	300
1	-78	189
3	-75	141
7	291	-252
H= 14, K= 6		
-10	-81	10
-8	-73	147
-6	244	-232
-4	-77	-93
-2	216	-190
0	295	-247
2	328	-290
4	253	-205
6	346	-281
H= 15, K= 6		
-9	-76	-4
-7	144	-178
-5	-73	55
-3	-75	202
-1	-75	-116
1	-73	-59
3	-74	52
5	-76	81
H= 16, K= 6		
-8	149	85
-6	195	194
-4	217	161
-2	449	393
0	251	196
2	298	248
4	326	256
H= 17, K= 6		
-7	-76	151
-5	-75	-84
-3	178	-203
-1	144	-84
1	-75	-26
3	-76	-57
H= 18, K= 6		
-6	279	-274
-4	214	-194
-2	373	-299
0	307	-261
2	194	-134
H= 19, K= 6		
-3	-77	-184
-1	-77	-82
H= 0, K= 7		
1	328	355
3	533	531
5	-80	77
7	276	267
9	133	139
11	-81	141
H= 1, K= 7		
-10	256	-211
-8	181	-217
-6	213	-292
-4	-79	-99
-2	-77	49
0	-77	141
2	-77	-31
4	442	-440
6	-80	-104
8	255	-250
10	505	-465
H= 2, K= 7		
-11	-81	-98
-9	237	-243
-7	489	-504
-5	601	-588
-3	488	-442
-1	425	-437
1	223	-208
3	165	-143
5	187	216
7	120	-113
9	-80	-63
11	170	-148
H= 3, K= 7		
-10	145	-60
-8	-81	-74
-6	316	305
-4	-79	-48
-2	-78	137
0	346	371
2	509	553
4	816	783
6	268	306
8	275	259
10	270	214
H= 4, K= 7		
-11	-81	139
-9	375	344
-7	255	249
-5	495	497
-3	-79	59
-1	-78	75
1	-78	82
3	293	300
5	208	246
7	134	192
9	146	96
H= 5, K= 7		
-10	-80	122
-8	-80	-144
-6	241	-290
-4	-80	-36
-2	421	-433
0	792	-786
2	690	-669
4	210	-231
6	293	-290
8	327	-335
10	-81	82
H= 6, K= 7		
-11	-81	-119
-7	-77	-108
-5	176	-214
-3	158	178
-1	201	-213
1	285	-269
3	147	-162
5	378	-388
7	225	-239
9	220	-181
H= 7, K= 7		
-10	-80	142
-8	439	435
-6	331	365
-4	565	573
-2	602	615
0	287	157
2	-81	130
4	-78	97
6	181	165
8	-80	62
H= 8, K= 7		
-11	-81	112
-9	-80	72
-7	-75	1
-5	204	221
-3	302	349
-1	144	179
1	-80	44
3	-79	106
5	374	341
7	-80	161
9	258	259
H= 9, K= 7		
-10	292	-319
-8	274	-285
-6	169	-217
-4	385	-429
-2	-80	-174
0	-80	-59
2	-78	37
4	-75	12
6	208	-187
8	-81	-8
H= 10, K= 7		
-9	150	-129
-7	313	-306
-5	121	-126
-3	227	-222
-1	-79	-126
1	183	-216
3	170	-162
5	330	-297
7	222	-181
H= 11, K= 7		
-10	127	251
-6	-73	99
-4	289	292
-2	-77	-36
0	-77	-88
2	-75	-79
4	-73	82
6	152	130
H= 12, K= 7		
-9	-76	127
-7	210	229
-5	-73	84
-3	468	439
-1	244	228
1	283	300
3	295	261
5	-75	31
H= 13, K= 7		
-8	108	32
-6	147	-102
-4	177	-93
-2	-73	109
2	315	-286
4	359	-312
H= 14, K= 7		
-7	153	-240
-5	149	-183
-3	180	-217
-1	233	-217
1	211	-190
3	-75	-57
H= 15, K= 7		
-6	-76	32
-4	125	-203
-2	226	181
0	436	388
2	300	285
H= 16, K= 7		
-5	154	138
-3	-76	-52
-1	-76	-39
H= 17, K= 7		
-2	220	-223
H= 0, K= 8		
0	295	321
2	412	453
4	224	240
6	106	74
8	264	-228
H= 1, K= 8		
-9	-81	-109
-5	314	-294
-3	472	-449
-1	419	-497
1	327	-375
3	-78	-12
5	-75	-146
7	366	-329
9	-81	-29
H= 2, K= 8		
-8	-80	-119
-6	314	-307
-4	152	-105
-2	290	-275
0	-79	-61
2	177	181
4	-76	171
6	-73	-81
H= 3, K= 8		
-9	225	296
-7	254	294
-5	315	316
-3	444	450
-1	-79	151
1	-78	74
3	-77	141
5	173	156
7	213	151
H= 4, K= 8		
-8	240	247
-6	131	112
-4	-76	62
-2	-78	-68
0	399	-412
2	403	-385
4	-74	-46
6	-73	-68
8	-81	58
H= 5, K= 8		
-9	165	-165
-5	252	-254
-3	196	-250
-1	-77	-127
1	-77	-73
3	156	-229
5	254	-233
7	-75	-39
H= 6, K= 8		
-8	-75	-31
-6	144	124
-4	-75	70
-2	121	203
0	-77	12
2	-75	55
4	-72	1
6	-75	105
H= 7, K= 8		
-9	-77	97
-7	-74	58
-5	183	174
-3	-75	73
-1	-76	113
1	-75	94
3	245	225
5	336	268
7	192	150
H= 8, K= 8		
-8	-76	-19
-6	-74	-166
-4	-73	-21
-2	-74	-143
0	207	67
2	-72	71
4	181	133
6	154	101
H= 9, K= 8		
-5	147	-163
-3	-72	-5
-1	129	-150
1	402	-361
3	351	-309
H= 10, K= 8		
-8	-77	58
-6	-75	-29
-4	-74	-21
0	144	-180
2	236	-234
4	-76	-148
H= 11, K= 8		
-7	248	229
-5	151	132
-3	212	255
-1	411	374
1	282	225
3	153	158
H= 12, K= 8		
-6	-77	73
-4	-75	32
-2	-75	143
0	-75	78
2	-76	96
H= 13, K= 8		
-5	157	-183
-3	190	-211
-1	189	-165
1	156	-169
H= 14, K= 8		
-2	-77	-124
H= 0, K= 9		
1	287	-292
3	224	-165
5	171	-196
H= 1, K= 9		
-6	110	-28
-4	239	-240
0	145	-150
2	235	-242
4	-75	-89
6	-77	109
H= 2, K= 9		
-5	107	49
-1	204	224
1	209	166
3	-74	113
5	189	213
H= 3, K= 9		
-6	247	256
-2	-74	-16
0	-73	-69
2	183	-135
6	112	25
H= 4, K= 9		
-5	153	-180
-3	213	-231
-1	147	-107
1	-74	-98
5	157	63
H= 5, K= 9		
-6	111	-76
-4	-75	40
0	-74	26
2	-75	112
4	219	207
H= 6, K= 9		
-5	-76	2
-3	-75	115
-1	-75	29
1	-75	27
3	-76	91
H= 7, K= 9		
-2	-75	-43
0	-75	0
2	-76	-25
H= 8, K= 9		
-5	112	20
-3	-76	49
-1	-74	-130
1	269	-227
3	194	-210
H= 9, K= 9		
-4	-77	-11
-2	-76	-98
0	109	-91
H= 10, K= 9		
-1	274	233

[a] The values of *h* and *k* are given above each group with the values of *l*, 10*F*(obsd), and 10*F*(calcd) given in that order. A negative *F*(obsd) indicates an unobserved reflection.

TABLE II

Position and Thermal Parameters ($\times 10^4$) with Their Estimated Standard Deviations in Parentheses[a]

Atom[b]	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	2500[c]	1587 (2)	0[c]	26 (1)	137 (3)	56 (1)	0[c]	19 (1)	0[c]
O1	2500[c]	−2488 (19)	0[c]	65 (7)	175 (27)	166 (17)	0[c]	−32 (17)	0[c]
N	2500[c]	−1228 (16)	0[c]	32 (4)	104 (22)	83 (12)	0[c]	−2 (10)	0[c]
P	3426 (1)	2602 (3)	405 (2)	24 (1)	113 (4)	49 (1)	0 (2)	17 (2)	1 (4)
O2	2505 (4)	−531 (11)	694 (6)	40 (3)	196 (15)	65 (5)	8 (10)	32 (6)	66 (15)
CA1	4046 (5)	1371 (12)	811 (6)	27 (3)	122 (15)	45 (5)	16 (10)	18 (6)	19 (15)
CA2	4543 (5)	1756 (14)	1439 (7)	27 (3)	190 (20)	55 (6)	22 (13)	22 (7)	8 (19)
CA3	5020 (5)	734 (20)	1692 (9)	22 (3)	291 (29)	70 (8)	−6 (16)	21 (8)	28 (26)
CA4	4996 (6)	−585 (18)	1342 (10)	33 (4)	214 (25)	82 (9)	66 (16)	41 (10)	83 (25)
CA5	4486 (6)	−1003 (15)	707 (11)	26 (3)	181 (21)	114 (11)	56 (13)	39 (10)	92 (24)
CA6	4020 (6)	−25 (14)	449 (8)	33 (3)	177 (19)	63 (7)	7 (13)	36 (8)	−5 (18)
CB1	3416 (4)	3851 (11)	1312 (6)	16 (2)	128 (15)	46 (5)	9 (8)	15 (5)	12 (13)
CB2	3304 (5)	3275 (13)	2101 (7)	25 (3)	185 (19)	51 (6)	16 (12)	17 (6)	2 (18)
CB3	3230 (6)	4240 (16)	2777 (8)	33 (3)	218 (24)	48 (6)	29 (15)	30 (7)	−5 (20)
CB4	3241 (6)	5693 (15)	2670 (8)	29 (3)	170 (20)	62 (7)	16 (13)	19 (7)	−22 (19)
CB5	3351 (6)	6288 (13)	1881 (8)	36 (3)	145 (17)	54 (6)	−17 (12)	13 (7)	−30 (18)
CB6	3447 (5)	5356 (11)	1213 (7)	30 (3)	113 (16)	53 (6)	−35 (10)	22 (7)	−24 (15)
CC1	3695 (5)	3707 (10)	−422 (6)	24 (3)	107 (14)	41 (5)	7 (9)	8 (5)	−3 (13)
CC2	3265 (5)	4423 (13)	−1023 (7)	27 (3)	157 (18)	56 (6)	−17 (12)	10 (7)	46 (17)
CC3	3424 (6)	5280 (15)	−1688 (9)	33 (4)	218 (24)	74 (8)	10 (14)	28 (9)	76 (22)
CC4	4008 (7)	5331 (14)	−1767 (10)	45 (5)	153 (20)	81 (9)	19 (15)	36 (10)	72 (21)
CC5	4450 (5)	4587 (14)	−1183 (9)	24 (3)	197 (21)	83 (8)	−4 (13)	34 (8)	5 (22)
CC6	4296 (5)	3790 (13)	−505 (9)	27 (3)	143 (17)	84 (8)	16 (11)	43 (8)	49 (18)

Probable Hydrogen Positions ($\times 10^3$)

Atom[d]	x	y	z	Atom[d]	x	y	z
HA2	456	275	184	HB5	343	745	186
HA3	523	117	211	HB6	347	593	056
HA4	530	−117	141	HC2	275	438	−108
HA5	454	−235	077	HC3	312	573	−221
HA6	369	000	−024	HC4	400	610	−211
HB2	323	196	207	HC5	597	471	−122
HB3	311	394	342	HC6	449	301	−026
HB4	314	659	331				

[a] The temperature factor is of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] See Figure 1 for the atom-labeling scheme. [c] Parameter determined by space group symmetry. [d] An isotropic B of 6.0 Å^2 was used in the structure factor calculation.

space group I2/a there is an eightfold set of general positions $(0, 0, 0; {}^1/_2, {}^1/_2, {}^1/_2) \pm (x, y, z; {}^1/_2 - x, y, \bar{z})$, one fourfold set of special positions with symmetry C_2 $(0, 0, 0; {}^1/_2, {}^1/_2, {}^1/_2) \pm ({}^1/_4, y, 0)$, and four fourfold sets of special positions of point symmetry C_i. With four nondisordered molecules of the complex in the unit cell, the space group symmetry requires the Cu, N, and at least one O atom to lie on the twofold rotation axis. A sharpened three-dimensional Patterson function with the origin removed yielded positional parameters for the above atoms along with the P atom. The remainder of the structure was solved and refined by use of three-dimensional electron density maps to a conventional R of 0.19 ($R = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$). The structure was refined by full-matrix least-squares methods on an IBM 360/75 computer including anisotropic thermal parameters to an R of 0.084. The weighting scheme used was $\sqrt{w} = 1$ if $F_o \leq 42.4$ and $\sqrt{w} = 42.4/F_o$ if $F_o > 42.4$, where F_o is on the same scale as in Table I. A difference electron density function calculated at this point indicated reasonable position parameters for the 15 phenyl H atoms. An additional two cycles of least-squares refinement, in which the hydrogen atoms were included in the structure factor calculation but were not refined, gave a final R of 0.074. Atomic parameter shifts for the last cycle of refinement were less than 1×10^{-5} of a cell edge. A final three-dimensional difference electron density map was essentially featureless. Atomic scattering factors for Cu, P, O, N, C, and H used in all of the calculations were taken from ref 5. The Cu and P scattering factors were corrected for the real part of the anomalous dispersion.[6] Final observed and calculated structure factors are listed in Table I. Table II contains the final position and thermal parameters of all atoms along with the estimated standard deviations. Intramolecular distances, angles, and their standard deviations were calculated from the refined parameters[7] and are listed in Tables III and IV. Table IV also contains the least-squares planes through the carbon atoms of the benzene rings. All intermolecular distances are greater than or equal to the sum of their van der Waals radii and are not included in the tabulation. The C–H distances (average value 1.1 ± 0.2 Å) and the C–C–H angles (average value 119 ± 2°) are not listed.

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(5) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 201.

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

(7) M. E. Pippy and F. R. Ahmed, "Scan of Interatomic Distances and Angles," Report NRC-12, National Research Council of Canada, Ottawa, Canada, 1967.

TABLE III

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (DEG) FOR THE COPPER AND NITROGEN ATOMS[a–c]

Atoms	Distance	Atoms	Angle
Cu–P	2.256 (3)	P–Cu–P′	131.2 (1)
Cu–O2	2.22 (1)	P–Cu–O2	114.3 (3)
Cu–N	2.59 (2)	O2–Cu–O2′	57.5 (3)
N–O1	1.16 (2)	P–Cu–O2′	108.3 (3)
N–O2	1.25 (1)	O2–N–O2′	118.2 (4)
O2–O2′	2.14 (1)	O2–N–O1	121 (1)
		Cu–O2–N	92.2 (6)

[a] See Figure 1 for the atom-labeling scheme. [b] Numbers in parentheses are estimated standard deviations. [c] Primed atoms are related by a twofold axis to unprimed atoms.

TABLE IV

DIMENSIONS OF THE TRIPHENYLPHOSPHINE GROUP[a–c]

Atoms	Length, Å	Atoms	Angle, deg	Atoms	Angle, deg
P–CA1	1.81 (1)	Cu–P–CA1	116.4 (4)	CA1–P–CB1	104.9 (5)
P–CB1	1.82 (1)	Cu–P–CB1	108.8 (3)	CA1–P–CC1	104.4 (5)
P–CC1	1.83 (1)	Cu–P–CC1	117.0 (3)	CB1–P–CC1	104.1 (5)

Best Plane Equation through Ring A

$$-0.6018X - 0.3383Y + 0.7234Z = -4.868$$

Distances (Å) of carbon atoms from plane

CA1	−0.005	CA3	0.001	CA5	0.004
CA2	0.004	CA4	−0.005	CA6	0.001

Atoms	Length, Å	Atoms	Angle, deg
CA1–CA2	1.37 (2)	P–CA1–CA2	123.2 (8)
CA2–CA3	1.42 (2)	CA1–CA2–CA3	119 (1)
CA3–CA4	1.32 (2)	CA2–CA3–CA4	122 (1)
CA4–CA5	1.41 (2)	CA3–CA4–CA5	120 (1)
CA5–CA6	1.38 (2)	CA4–CA5–CA6	120 (1)
Ca6–CA1	1.40 (2)	CA5–CA6–CA1	121 (1)
		CA6–CA1–CA2	119 (1)
		CA6–CA1–P	118.0 (8)

Best Plane Equation through Ring B

$$0.9265X - 0.0124Y + 0.3760Z - 7.460$$

Distances (Å) of carbon atoms from plane

CB1	−0.005	CB3	0.016	CB5	−0.008
CB2	−0.010	CB4	−0.008	CB6	0.014

Atoms	Length, Å	Atoms	Angle, deg
CB1–CB2	1.40 (2)	P–CB1–CB2	117.7 (8)
CB2–CB3	1.41 (2)	CB1–CB2–CB3	118 (1)
CB3–CB4	1.35 (2)	CB2–CB3–CB4	122 (1)
CB4–CB5	1.40 (2)	CB3–CB4–CB5	120 (1)
CB5–CB6	1.39 (2)	CB4–CB5–CB6	119 (1)
CB6–CB1	1.40 (1)	CB5–CB6–CB1	121 (1)
		CB6–CB1–CB2	120 (1)
		CB6–CB1–P	122.4 (8)

Best Plane Equation through Ring C

$$0.0116X + 0.8011Y + 0.5984Z = 2.440$$

Distances (Å) of carbon atoms from plane

CC1	0.007	CC3	0.017	CC5	−0.011
CC2	−0.019	CC4	−0.002	CC6	0.009

Atoms	Length, Å	Atoms	Angle, deg
CC1–CC2	1.37 (2)	P–CC1–CC2	116.9 (8)
CC2–CC3	1.40 (2)	CC1–CC2–CC3	121 (1)
CC3–CC4	1.35 (2)	CC2–CC3–CC4	119 (1)
CC4–CC5	1.38 (2)	CC3–CC4–CC5	121 (1)
CC5–CC6	1.38 (2)	CC4–CC5–CC6	120 (1)
CC6–CC1	1.39 (2)	CC5–CC6–CC1	120 (1)
		CC6–CC1–CC2	119 (1)
		CC6–CC1–P	124.1 (8)

[a] See Figure 1 for the atom-labeling scheme. [b] Numbers in parentheses are estimated standard deviations. [c] Least-squares planes were calculated with reference to an orthogonal coordinate system where X, Y, Z refer to a, b, c^*.

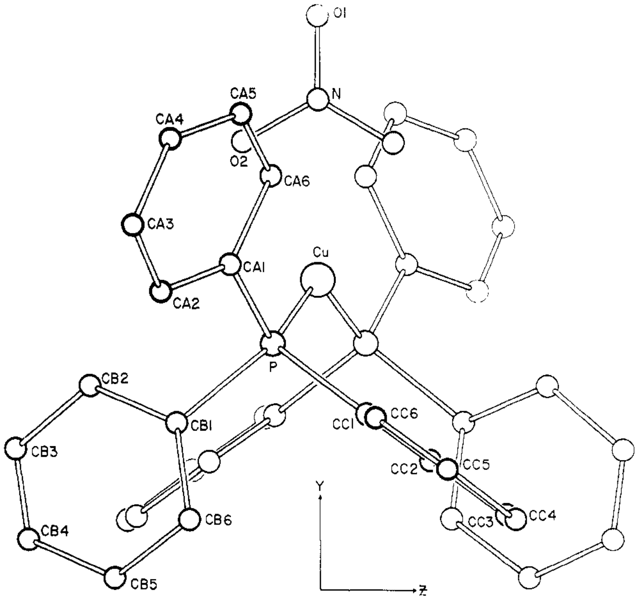

Figure 1.—A view of bis(triphenylphosphine)copper(I) nitrate showing the molecular geometry and atomic numbering. The O1, N, and Cu atoms lie on a twofold axis passing through the molecule. The phenyl hydrogens are not shown.

Results and Discussion

The crystal structure consists of discrete molecules of bis(triphenylphosphine)copper(I) nitrate separated by van der Waals distances. A view of the molecule is given in Figure 1 which shows the coordination geometry of the copper atom. The Cu–O2 distance of 2.22 ± 0.01 Å is longer than 1.83 Å which is the sum of the covalent radii of 1.17 Å for Cu(I)[8] and 0.66 Å for O.[9] The long Cu–N distance of 2.59 ± 0.02 Å precludes any significant bonding between these two atoms. These distances indicate the poor coordinating properties of the NO_3^- ion, a fact that has been mentioned by others.[1,2]

Using the significance tests suggested by Cruickshank and Robertson,[10] the Cu–P distance of 2.256 ± 0.003 Å is significantly shorter than the Cu–P distance of 2.276 ± 0.001 Å found in borohydridobis(triphenylphosphine)copper(I) by Lippard and Melmed.[11] Both Cu–P distances are significantly longer than the distances of 2.238 and 2.222 Å (both ±0.005 Å) found in phenylethynyl(trimethylphosphine)copper(I) by Corfield and Shearer.[12] The P–Cu–P angle of 131.2 ± 0.1° in the nitrate differs greatly from the tetrahedral value of 109.47° and is the largest angle yet observed in formally tetrahedral Cu(I) compounds. Truter and Rutherford[13] had attributed the large S–Cu–S angle of 112.3 ± 0.1° found in tetrakis(thioacetamide)copper(I) chloride to hydrogen bonding, unlikely in our structure. Furthermore, Lippard and Melmed[11] observed

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[8] N. C. Baenziger, H. L. Haight, and J. R. Doyle, *Inorg. Chem.*, **3**, 1535 (1964).

[9] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

[10] D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, **6**, 698 (1953).

[11] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967).

[12] P. W. R. Corfield and H. M. M. Shearer, *Acta Cryst.*, **21**, 957 (1966).

[13] M. R. Truter and K. W. Rutherford, *J. Chem. Soc.*, 1748 (1962).

a P–Cu–P′ angle of 123.26 ± 0.06° in the borohydrido complex and suggested that the distortion may be due to a combination of steric repulsions and Cu–B bonding. Corfield and Shearer,[12] however, found a P–Cu–P′ angle of 123.8 ± 0.2° with a significantly shorter Cu–P bond length and suggested that the shortening may have been due to Cu–P π bonding. In phenylethynyl(trimethylphosphine)silver(I)[14] the Ag–P bond length of 2.490 ± 0.004 Å is considerably shorter than the sum of the covalent radii (2.62 Å);[9] however, the P–Ag–P angle is only 118.4 ± 0.2° which is smaller than that in either the nitrato or the borohydrido complex. By comparison the P–Ni–P angle in dibromobis(triphenylphosphine)nickel(II)[15] is 110.4 ± 0.2°, with an Ni–P bond length of 2.333 ± 0.005 Å which is similar to the Cu–P bond lengths, indicating that smaller P–M–P angles are possible at the observed M–P distances.

The large P–Cu–P angles in the three complexes cannot be rationalized on the basis of steric repulsions, although it is difficult to separate steric effects from σ- or π-bonding effects. Moreover, a comparison of the borohydrido and nitrato complexes suggests that the anion has an important role in determining the Cu–P distance and the P–Cu–P angles. The dependence of the Cu–P distance and P–Cu–P angle on the anion may be related to the geometry or the donor properties of the anion. Both NO_3^- and BH_4^- have a relatively small "bite," with the O–Cu–O′ angle of 57.5 ± 0.3° in the present structure being a result of the constrained geometry of the nitrate ion. The better donor properties of NO_3^- relative to BH_4^- may increase the back-bonding with a resulting decrease in the Cu–P distance and an increase in the P–Cu–P angle. Further studies on copper(I)–phosphine complexes are in progress in an attempt to distinguish between the steric and electronic effects in Cu(I)–P bonds.

The geometry of the coordinated nitrate anion is given in Table III. The N–O2 bond length of 1.25 ± 0.01 Å agrees well with the value of 1.241 ± 0.002 Å reported by Cherin, Hamilton, and Post[16] and the average of 1.263 Å for coordinated nitrate reported by Taylor, Mueller, and Hitterman.[17] The N–O1 bond distance of 1.16 ± 0.02 Å has not been corrected for significant thermal motion. An approximate thermal correction of 0.07 Å was computed by the method of Leung and Marsh.[18] However, in the absence of absorption corrections we do not feel justified in an extensive discussion of the thermal parameters or the corrections calculated from these parameters. The corrected N–O1 bond distance of 1.23 Å is reasonable but presented with the above reservations. The O–N–O angles are close to the expected value of 120°. The dihedral angle between the P–Cu–P′ and NO_3^- plane is 96° which indicates a slight rotation of the nitrate ion with respect to the idealized geometry. A similar effect was observed in the BH_4^- complex.[11] All of the intermolecular distances less than 4.0 Å were calculated. Because of the bulky triphenylphosphine groups, the majority of the intermolecular contacts involve the hydrogen atoms. In no case were any short intermolecular contacts found.

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