Crystal and Molecular Structure of Potassium Acetylacetonate Hemihydrate

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The crystal structure of potassium acetylacetonate hemihydrate, $KC_5H_7O_2 \cdot 1/2H_2O$, has been determined by X-ray diffraction method. Crystals are triclinic with space group $P\bar{1}$, $a=10.86$, $b=8.74$, $c=7.45$ Å, $\alpha=90.5$, $\beta=95.8$, $\gamma=91.9°$, and $Z=4$. The final R value was 0.109 for 1589 visually estimated reflection data. Each potassium ion is surrounded by seven oxygen atoms, at distances of 2.65 to 3.05 Å, six of which belong to four acetylacetone anions and the rest is a water molecule. The bond lengths and angles of the acetylacetone anion are very similar to those of acetylacetone groups in heavy metal chelates, but differ from those of the free molecule of acetylacetone.

A number of crystal-structure determination of transition metal complexes of acetylacetone[1-6] revealed that the chelate ring is nearly planar and the molecular dimension of the ring is almost independent of the kind of the metal atom. It is, therefore, particularly interesting to compare the structure of a free acetylacetone anion with that of acetylacetone coordinated to heavy metals. The crystal structure of potassium acetylacetonate hemihydrate, $KC_5H_7O_2 \cdot 1/2H_2O$ (hereafter denoted as PAH), is described in this paper.

Experimental

The samples of PAH were prepared by mixing hot alcoholic solution of potassium hydroxide and 2,4-pentanedione,[7] and single crystals were obtained in the form of rods. They are hygroscopic; the specimens were sealed in thin-walled glass capillary tubes. The crystal was found to be triclinic from Weissenberg photographs. The unit cell dimensions were determined on the basis of the high-angle reflections on Weissenberg photographs taken with Cu$K\alpha$ radiation ($\lambda=1.5418$ Å) as follows: $a=10.86\pm0.01$, $b=8.74\pm0.02$, $c=7.45\pm0.02$ Å, $\alpha=90.5\pm0.4$, $\beta=95.8\pm0.4$, and $\gamma=91.9\pm0.4°$. They were calibrated by using the reference lines of sodium chloride ($a=5.6396$ Å). The measured density was 1.40 g cm^{-3} (flotation method in carbon tetrachloride and cyclohexane), while the calculated one was 1.39 g cm^{-3} for $Z=4$. The intensities were recorded on multiple-film equi-inclination Weissenberg photographs with Cu$K\alpha$ radiation. Intensities of the layers $hk0$–$hk4$ were collected and estimated visually. The absolute scale of the structure amplitudes for each layer was obtained at a later stage by correlating with the calculated ones. In total, 1590 reflections were observed. Corrections for Lorentz and polarization effects were applied in the usual way. Correction for absorption was neglected. The space group $P\bar{1}$ was assumed at the outset and confirmed in the course of refinement.

Structure Determination

The structure analysis was initiated on the basis of the two-dimensional heavy-atom method. The x and y coordinates of two independent potassium ions were deduced from a Patterson projection onto the (001) plane; they were overlapped in the Fourier projection on this plane. Iterative Fourier and difference-Fourier syntheses refined the x and y coordinates of K, O and C atoms. The results suggested that the acetylacetone groups are almost planar and parallel to the (001) plane. The z coordinates of the atoms were guessed from a packing consideration. With the trial and error method, all the atoms in the two planar anions and the oxygen

Table 1. Positional and thermal parameters[a] with their estimated standard deviations ($\times 10^4$)

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K(1)	4915(3)	1931(3)	80(5)	60(2)	73(3)	90(11)	1(4)	1(7)	−26(8)
O(11)	3292(8)	3137(10)	2294(15)	57(8)	95(13)	196(36)	11(16)	−23(24)	−14(30)
O(12)	3691(8)	−132(10)	2477(15)	48(8)	95(13)	176(34)	−3(15)	0(23)	3(29)
C(11)	1235(15)	3825(19)	1145(30)	91(17)	146(27)	371(73)	106(34)	−97(52)	−35(64)
C(12)	2209(11)	2687(14)	1763(21)	55(11)	92(18)	98(49)	12(22)	−10(32)	−86(40)
C(13)	1816(12)	1101(16)	1601(23)	49(11)	138(22)	131(52)	21(25)	15(34)	−18(47)
C(14)	2548(11)	−165(14)	1963(22)	50(11)	78(17)	153(51)	−8(21)	10(32)	−17(40)
C(15)	1930(14)	−1760(17)	1654(28)	80(15)	103(21)	334(67)	−90(29)	30(46)	−64(55)
K(2)	4909(3)	1939(3)	4941(5)	62(2)	76(4)	103(11)	3(5)	−9(7)	−5(8)
O(21)	6379(8)	15(10)	2528(15)	55(8)	94(13)	190(35)	10(16)	−28(24)	−44(30)
O(22)	6424(9)	3310(10)	2664(15)	80(9)	97(13)	126(34)	27(17)	−29(25)	−80(29)
C(21)	8303(15)	−1129(17)	3405(28)	93(16)	114(22)	296(66)	100(31)	−28(47)	−40(55)
C(22)	7516(11)	243(15)	3060(20)	53(11)	111(19)	40(46)	23(23)	−4(30)	−23(40)
C(23)	8081(11)	1687(15)	3456(23)	45(11)	111(20)	184(54)	−30(23)	−8(34)	−54(46)
C(24)	7520(11)	3101(15)	3237(23)	48(11)	93(18)	186(54)	−38(22)	4(34)	−24(44)
C(25)	8334(19)	4474(19)	3960(35)	137(23)	113(25)	560(91)	−164(39)	40(69)	−172(73)
O(w)	4909(9)	5734(10)	2489(15)	95(10)	91(13)	116(34)	25(18)	29(26)	−31(29)

a) Thermal factors refer to the expresion $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

TABLE 2. OBSERVED AND CALCULATED STRUCTURE FACTORS ($\times 10$)
Asterisks indicate reflections with $w=0.5$, otherwise $w=1.0$.

H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC
K,L= 0 0	5 178 162	6 53 -15	5* 0 34	K,L= 3 1	6* 31 8	9 106 -85	-12* 0 29	-4 330 284
2 99 -72	6 148-152	K,L= 10 0	6* 0 2	-9* 50 -53	7* 31 -30	10 139 124	-11* 0 -16	-3 342-302
3 684-755	7 183-191	-6 103 113	7 55 57	-8 64 64	K,L= -8 2	11 81 -85	-10 78 -67	-2 326 281
4 385 397	8 61 63	-5 132-139	8 64 -63	-7* 0 -16	-9 78 112	12 121 116	-9 94 74	-1 319-264
5 294-240	9 190 181	-4 78 86	9 60 69	-6* 0 -10	-8 112-126	K,L= -3 2	-8 98 -66	0 299 277
6 608 572	10 135-118	-3 102 -99	K,L= -2 1	-5 109-126	-7 109 113	-13 53 78	-7* 23 -16	1 250-207
7 629-543	11* 0 20	-2 135 132	-8* 50 35	-4 67 66	-6 106-128	-12 112-125	-6 141 132	2 313 283
8 372 352	12 61 -62	-1 165-171	-7 66 -77	-3* 0 -15	-5 78 95	-11 67 71	-5 94 -91	3 297-290
9 228-205	K,L= 5 0	0 164 171	-6 72 -67	-2 202 176	-4 116-123	-10* 0 -20	-4 155 138	4 211 190
10 103 84	-12 55 55	1 106-110	-5* 47 -42	-1 90-108	-3 187 194	-9 202 198	-3 329-277	5 288-320
11 69 -55	-11 56 -67	2 72 64	-4 180 199	0 209 229	-2 146-128	-8 322-321	-2 396 321	6 248 261
12 135 127	-10 146 136	3 83 -78	-3 67 -80	1 184-164	-1 136 120	-7 266 250	-1 178 -99	7* 0 -45
13 119-115	-9 220-211	4 98 109	-2 273 274	2 93 -98	0 225-206	-6 326-303	0 52 -34	8 79 83
K,L= 1 0	-8 267 264	5 63 -61	-1 73 -38	3 85 -93	1 199 181	-5 377 365	1 464-452	9 112-111
-13* 0 32	-7 264-241	K,L= 11 0	0 310-298	4 79 78	2 146-129	-4 183-171	2 440 429	10 81 74
-12 98 -75	-6 281 275	-2 58 71	1 154-128	5* 0 23	3 143 139	-3 56 -1	3 252-227	11 117-119
-11 146 133	-5 302-284	-1 54 -55	2 213 244	6 109 120	4 132-132	-2 330-273	4 531 526	K,L= 6 2
-10 73 -17	-4 308 272	0 82 100	3 237-250	7 97-115	5 78 87	-1 745 651	5 442-393	-11* 45 -46
-9 80 -64	-3 384-370	1 66 -70	4 206 221	8* 0 -14	6 81 -84	0 757-765	6 135 136	-10* 50 49
-8* 33 9	-2 445 409	2* 49 41	5* 48 -48	9 56 61	7 108 95	1 661 679	7 141-140	-9* 0 -21
-7* 0 -3	-1 477-463	K,L= -8 1	6* 0 15	K,L= 4 1	8 93 -90	2 132-148	8 125 94	-8 61 -74
-6 175-139	0 494 460	-3* 49 -52	7 78 81	-8* 50 -60	9 91 110	3 65 -36	9 176-162	-7* 0 -6
-5 185 165	1 449-405	-2* 0 -16	8 57 -47	-7* 0 45	K,L= -7 2	4 331-303	10 227 250	-6 95 92
-4 69 60	2 413 404	-1 75 75	9 124-128	-6* 0 7	-10* 12 24	5 171 169	11 144-141	-5 97 -70
-3 117 73	3 331-292	0* 0 -9	10 91 95	-5 113 124	-9* 15 19	6 122-114	12 66 73	-4 283 238
-2 145-125	4 298 273	1 54 45	K,L= -1 1	-4* 18 -20	-8 53 -55	7 394 395	13 95-108	-3 372-342
-1 238-241	5 244-238	2 68 -60	-12* 40 46	-3 108-118	-7 125 132	8 284-269	K,L= 2 2	-2 167 144
0 397 531	6 138 116	3* 0 -24	-11* 0 -1	-2 64 -51	-6 102 -98	9* 0 -8	-13 88 101	-1 85 61
1 219-211	7 218-220	4* 26 31	-10 66 -83	-1 182 188	-5* 0 4	10* 0 -3	-12 125-137	0* 0 21
2 183-157	8 254 258	5* 0 -6	-9* 46 35	0 248-264	-4 123-103	11 105 86	-11* 0 45	1 278-257
3 192-189	9 122-115	6 60 -57	-8* 46 55	1 71 65	-3 157 151	12* 42 -43	-10 93 -90	2 291 270
4 137 124	10 88 85	7 64 73	-7 116-102	2 140 133	-2* 0 13	K,L= -2 2	-9 296 303	3 273-254
5 67 58	11 70 -68	K,L= -7 1	-6 103 102	3* 0 10	-1 134 127	-13* 41 40	-8 287-293	4 279 299
6 268 246	K,L= 6 0	-3 53 56	-5* 49 50	4 66 -44	0 440-400	-12* 0 19	-7 287 273	5 163-170
7 376-313	-11 91 82	-2* 49 -40	-4 60 -42	5* 0 8	1 195 191	-11* 0 -25	-6 386-370	6 94 85
8 239 214	-10* 12 -36	-1* 35 -50	-3 108 129	6 97 -96	2 75 -60	-10 100 -94	-5 313 315	7 111-115
9 184-166	-9* 0 21	0 58 52	-2 351-403	7 107 106	3 239 239	-9 179 155	-4 297-294	8 94 93
10* 18 31	-8 66 69	1 72 -59	-1 163-183	8* 0 7	4 185-186	-8 170-156	-3 393 351	9 129-115
11* 35 -26	-7 138-137	2* 0 6	0 372 471	9 61 -59	5 96 87	-7 155 150	-2 535-472	10 170 172
12 134 126	-6* 0 -19	3* 37 40	1 65 85	K,L= 5 1	6 138-128	-6 163-161	-1 658 580	K,L= 7 2
13 106 -98	-5* 0 13	4* 0 8	2 177-233	-10* 49 -44	7 142 150	-5 199 209	0 665-559	-11* 49 75
K,L= 2 0	-4* 0 3	5* 38 -34	3 137 117	-9* 0 31	8 143-168	-4 253-237	1 601 575	-10 111-128
-13 108 113	-3 166 149	6* 26 41	4* 0 -15	-8 71 97	9 137 151	-3 350 317	2 454-430	-9 124 150
-12 107-111	-2* 0 20	K,L= -6 1	5 61 47	-7 65 -78	10 85 -99	-2 436-406	3 278 295	-8 146-182
-11 179 166	-1 360-319	-9* 44 -44	6* 0 -4	-6* 40 47	K,L= -6 2	-1 463 483	4 262-268	-7 125 147
-10 290-295	0 395 349	-8* 51 42	7 81 -68	-5* 38 -44	-11 97-126	0 562-562	5 171 163	-6 77 -76
-9 156 141	1 155-148	-7* 38 57	8 56 -55	-4 115-117	-10 118 125	1 560 587	6 107-101	-5 224 239
-8 85 -49	2* 17 -10	-6* 0 -1	9 60 54	-3 65 53	-9 129-125	2 527-492	7 180 153	-4 232-233
-7 328 289	3 57 -54	-5 65 -69	10* 42 24	-2 100 103	-8 108 103	3 237 254	8 244-253	-3* 0 -5
-6 319-298	4 95 92	-4* 0 4	K,L= 0 1	-1 90 -81	-7 84 -85	4 281-315	9 184 177	-2 242-230
-5 335 329	5 134-106	-3 68 -74	-12 57 -41	0 140 150	-6 127 133	5 346 353	10* 0 8	-1 397 427
-4 538-569	6 195 207	-2 120 122	-11* 0 35	1 135-144	-5 182-183	6 185-179	11* 0 0	0 150-132
-3 462 506	7 190-207	-1* 16 -9	-10* 47 54	2* 0 -1	-4 247 232	7 333 338	12* 31 -38	1 134 94
-2 381-403	8 150 139	0 76 -77	-9* 0 -21	3 63 55	-3 358-320	8 402-393	K,L= 3 2	2 219-221
-1 317 316	9 118-117	1* 0 18	-8* 0 -36	4* 29 35	-2 345 309	9 154 132	-13* 47 48	3 94 78
0 264-262	10* 44 66	2 98 101	-7* 50 47	5 94-102	-1 148-144	10 88 -93	-12 103 -96	4* 0 -9
1 306 288	11* 20 -34	3* 0 -33	-6 84 -73	6* 46 33	0 60 -41	11 142 130	-11* 20 -24	5 113 107
2 294-277	K,L= 7 0	4* 0 -9	-5* 0 0	7* 0 6	1* 48 -37	12 80 -84	-10 78 69	6 118-122
3 339 322	-11 80 108	5 59 -70	-4* 0 -12	8* 0 33	2 260 288	13 82 96	-9 222 213	7 109 107
4 303-276	-10 54 -80	K,L= -5 1	-3* 37 18	9 62 -57	3 243-221	K,L= -1 2	-8 308-302	8 81 -78
5 236 223	-9* 13 57	-9* 48 55	-2* 43 61	K,L= 6 1	4 199 146	-13* 29 -42	-7 129 107	K,L= 8 2
6 216-183	-8 90 -82	-8* 0 -2	1* 0 -3	-3 95 97	5 197-196	-12 91 111	-6 306-304	-9 81 80
7 119 102	-7 115 100	-7* 18 -19	2* 0 2	-2* 42 -44	6* 0 25	-11 202-217	-5 392 341	-8 86 -92
8* 10 6	-6 171-191	-6 85 -78	3* 0 3	-1 88 -87	7* 44 55	-10 200 191	-4 122 95	-7 79 90
9 98 -72	-5 191 195	-5 86 87	4* 29 -22	0* 50 57	8* 0 10	-9 166-164	-3* 42 14	-6 85 -98
10* 25 -48	-4* 25 -34	-4* 0 24	5 76 -73	1 84 71	9* 0 -8	-8 122 122	-2 481-413	-5 110 113
11 151 120	-3 214 203	-3 55 -42	6 70 57	2 86 -93	10 70 66	-7 87 -79	-1 658 651	-4 130-126
12* 0 -18	-2 295-288	-2 61 -59	7* 51 -66	3* 31 12	11 63 -53	-6 362 310	0 877-844	-3 132 116
13* 0 1	-1 118 -96	-1 121 130	8* 22 45	4 72 -71	K,L= -5 2	-5 452-419	1 527 514	-2 159-147
K,L= 3 0	0* 0 40	0 102 -95	9 79 75	K,L= 7 1	-12* 49 73	-4 311 277	2* 48 -49	-1 203 199
-13 57 48	1 268 264	1 147 134	10* 0 -11	-3 66 -39	-11 76 -78	-3 512-516	3 163 148	0 163-151
-12* 0 -3	2 124-108	2 71 -65	11 62 -66	-2* 32 -21	-10 117 121	-2 638 611	4 334-327	1 162 157
-11 54 62	3* 20 28	3 125-115	K,L= 1 1	-1 72 53	-9 63 -75	-1 213-157	5 199 184	2 204-206
-10 243-230	4 164-172	4* 37 41	-9 90 -83	0 79 -81	-8* 0 43	1 344-289	6 266-256	3 141 153
-9 145 133	5 78 90	5* 0 12	-8* 21 -5	1* 0 -1	-7 159-158	2 368 340	7 442 458	4 88-114
-8 160 137	6* 24 45	6* 18 -35	-7* 0 19	2 65 65	-6 199 215	3 68 -56	8 247-249	5 103 106
-7 84 72	7* 0 -23	7 111 125	-6 80 66	K,L= 8 1	-5 210-210	4 158 182	9* 0 52	6 102-108
-6 317-300	8* 9 13	8* 0 -30	-5* 0 1	-7 57 -73	-4 269 245	5 271-250	10 110-118	7 135 151
-5 104 109	9* 49 17	9* 36 -45	-4 54 26	-6* 0 32	-3 295-260	6 87 70	11 110 115	8 130-150
-4 458-500	10 78 -78	K,L= -4 1	-3 218-234	-5* 0 18	-2 346 286	7* 0 -30	12 76 -76	K,L= 9 2
-3 755 907	K,L= 8 0	-9* 46 47	-2 233 284	-4* 46 -54	-1 316-263	8 105 -95	K,L= 4 2	-5 77 -62
-2 596-431	-9 63 58	-8* 18 39	-1 227 236	-3* 0 -9	0 315 246	9 158 137	-13* 32 -82	-4 81 96
-1 137 112	-8 79 -79	-7 76 -88	0 414-425	-2* 0 42	1 256-243	10* 0 23	-12 78 95	-3* 30 -52
0 192 -47	-7 109 111	-6* 45 50	1 156-172	-1* 0 0	2 280 225	11 62 -34	-11 131-150	-2* 0 -19
1 199 217	-6 144-157	-5 66 -56	2 146 203	0 82 66	3 330-310	12* 0 -23	-10 90 102	-1 86 75
2 680-760	-5 168 163	-4 73 54	3 113 -85	1 58 -58	4 296 285	13* 0 11	-9* 0 -12	0 80 -86
3 752 875	-4 183-175	-3 89 90	4 131 129	K,L= 9 1	5 234-222	K,L= 0 2	-8 93 94	1* 42 28
4 465-485	-3 219 209	-2 82 -75	5* 35 25	-3 53 60	6 259 238	-13* 0 -18	-7 213-221	2* 0 15
5 331 318	-2 224-212	-1 139-129	6 117 -96	3 59 71	7 158-143	-12 109 98	-6 173 156	3* 0 -12
6 362-366	-1 179 165	0 216 225	7 113 123	K,L=-10 2	8 84 80	-11 164-177	-5 121-114	4* 0 -37
7 162 150	0 211-203	1 194-183	8* 17 -46	-5 54 -74	9 87 -92	-10 198 180	-4 320 275	5 63 69
8 75 -53	1 265 258	2 80 -85	9 80 -93	-4 68 86	10 122 121	-9 205-164	-3 265-209	6 70 -39
9 282 274	2 200-184	3 83 88	10* 50 48	-3 106-132	11 141-155	-8 83 77	-2 82 86	7 76 85

Table 2. (continued)

H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC
10 288-278	3 188 187	4 107 116	11* 35 28	-2 116 150	K,L= -4 2	-7* 28 -3	-1 118 -82
11 139 128	4 222-236	5* 0 2	K,L= 2 1	-1 93-102	-12 69 -82	-6 341 275	0 199-155
12 119-116	5 194 198	6* 0 8	-10 124-143	0 59 67	-11 62 63	-5 520-474	1 62 -32
13 89 104	6 167-177	7 75-100	-9 78 58	1 70 -90	-10 80 75	-4 289 257	2 275 274
K,L= 4 0	7 131 129	8* 0 -13	-8 62 64	2 93 116	-9* 0 16	-3 815-875	3 91 62
-12 53 58	8 84 -71	9* 18 44	-7* 20 -21	3 116-146	-8 253-263	-2 8551138	4* 0 -9
-11* 43 -49	9 92 101	K,L= -3 1	-6* 0 9	4 91 113	-7 126 113	-1 466 464	5 178-182
-10* 0 46	K,L= 9 0	-11* 34 41	-5 70 84	5* 48 -74	-6 76 77	1 550-883	6 133-122
-9 197-187	-8* 50 59	-9* 42 -41	-4 214-204	K,L= -9 2	-5 165 147	2 419 545	7 268 268
-8 211 213	-7 56 -59	-8* 45 -60	-3 251 285	-7 66 64	-4* 17 -12	3 454-454	8* 0 -49
-7* 0 -36	-6 73 75	-7 100 109	-2 327-329	-6 69 -75	-3 324-275	4 691 690	9 55 -43
-6* 0 0	-5* 25 -13	-6* 42 -30	-1 179-170	-5 57 65	-2* 0 13	5 414-387	10 77 -56
-5 145-154	-4 60 -44	-5 61 61	0 191 187	-4* 37 -25	-1 53 40	6 100 106	11 76 61
-4 122 67	-3* 43 30	-4 108-108	1 252 221	-3* 0 -18	0* 0 -1	7 96 -61	K,L= 5 2
-3 141 85	-2 65 38	-3 55 -58	2 59 -75	-2* 0 -4	1 110 79	8 146 112	-12 100 115
-2 199 163	-1 103 -76	-2 66 -53	3 199 213	-1 62 50	2 218 183	9 203-179	-11 108-123
-1 224-166	0 98 74	-1 227 194	4 174-183	0 86 -75	3 245-229	10 234 220	-10 105 111
0 165 147	1* 44 -14	0 103-135	5 69 -70	1 83 73	4 94 74	11 137-140	-9 83 -90
1 311-259	2 87 -69	1 238 236	6* 0 -41	2* 20 -5	5 195-184	12* 26 44	-8 120 118
2 287-226	3 91 78	2 65 -56	7 71 58	3 66 -66	6 267 279	13 75 -83	-7 142-154
3 229 223	4* 38 -49	3* 38 23	8* 0 -1	4 74 73	7 124-112	K,L= 1 2	-6 188 189
4 134 124	5* 0 16	4 168-179	9* 38 40	5* 34 -22	8* 0 -17	-13* 0 36	-5 281-262
5* 27 34	3 117 109	-8* 0 28	4 67 57	-7* 38 -32	2* 50 -22	2 121 119	-2 354-271
6* 43 -42	4 93 -74	-7 56 -41	5 55 48	-6* 41 -48	3 98 -86	3 94 -69	-1 286 249
K,L= -8 3	5* 0 16	-6* 0 -1	6 126-132	-5* 0 48	4 110 96	4 107 -90	0 190-153
-4* 30 -40	6 110-130	-5* 0 -16	7* 37 43	-4* 0 1	5 58 39	5 81 59	1 187 152
-3* 0 20	7 82 83	-4 54 31	K,L= 4 3	-3 123 118	6* 0 -13	6* 39 -74	2 251-219
-2 54 43	11 58 59	-3 68 66	-10* 0 -4	-2 187-178	7 150-150	7* 18 12	3 177 154
-1* 0 -4	K,L= -3 3	2* 0 15	-9* 32 -44	-1* 0 -15	8 114 140	8 120 112	4 176-165
0* 0 5	-12* 39 43	3* 43 -36	-8* 46 62	0* 0 26	9 52 -61	9* 0 -7	5 239 228
1 74 -55	-10* 43 -46	4* 0 -7	-6 100 93	1 170 151	10 91 79	10 104 -78	6 180-175
2* 0 7	-8 56 55	5* 41 24	-5 109-108	2 98-104	K,L= -3 4	11* 38 38	7* 18 21
3* 43 35	-7* 43 -24	6* 0 -32	-4* 0 2	3* 36 46	-12 75 -82	K,L= 0 4	8 59 64
4* 52 -41	-6* 0 31	7 71 66	-3* 0 -10	4 126-128	-11 170 179	-13 61 -90	9* 17 36
5* 0 5	-5 77 -65	8* 43 49	-2 115 97	5 120 149	-10 159-179	-12* 0 55	10 92 -82
6* 49 46	-4* 31 -11	9 91 -81	-1 277-256	6 104-116	-9 85 101	-11* 23 -56	K,L= 3 4
K,L= -7 3	-3* 35 23	K,L= 1 3	0 216 222	7 82 77	-8 122-132	-10 84 84	-11 152 166
-4* 45 49	-2* 51 48	-10 62 -60	1* 0 2	8 53 -51	-7 187 190	-9 159-168	-10 73 -82
-3 72 -75	-1 74 -58	-9 62 61	2* 23 32	K,L= -6 4	-6 145-166	-8 310 317	-9 70 -51
-2* 32 25	0 167 143	-8* 0 -6	3 100 -78	-10 54 61	-5 209 219	-7 308-310	-8 100 -91
-1* 0 -14	1* 47 -60	-7 84 71	4* 0 17	-9 89 -86	-4 392-431	-6 220 226	-7 113 110
0* 0 -14	2* 47 -41	-6 74 -78	5 89 -82	-8 104 120	-3 482 504	-5 430-406	-6* 17 8
1* 0 8	3 106 -81	-5* 0 28	6 152 149	-7 120-140	-2 346-322	-4 346 310	-5 233 230
2 72 52	4* 13 33	-4 120-130	7 90 -89	-6 118 130	-1 192 157	-3 140 79	-4 475-448
3* 46 -43	5* 50 41	-3 319 288	K,L= 5 3	-5 120-113	0 80 -49	-2 369 450	-3 397 374
K,L= -6 3	12* 43 -40	-2 162-130	-10 56 54	-4 83 74	1 221 192	1 280-368	-2 283-253
-7* 31 -42	K,L= -2 3	-1 247-181	-8* 45 -60	-3* 0 -16	2 441-449	2 399 463	-1 96 48
-6* 0 -15	-10* 31 26	0* 37 18	-6 80 -70	-2* 36 30	3 264 299	3 238-253	0 90 -52
-5* 0 -12	-8 54 -31	1 177 181	-5* 21 -22	-1 192-176	4 201-211	4 157 160	1 405 367
-4* 0 7	-7* 42 -26	2 121-140	-4 106 97	0 251 251	5 290 312	5 302-289	2 456-457
-3 66 59	-6 66 56	3 156 169	-3* 0 -6	1 104 -86	6 92 -93	6 380 375	3 309 314
-2* 0 -31	-5* 49 43	4 135-119	-2* 19 -26	2* 0 1	7 103 -71	7 325-326	4 340-362
-1 67 -65	-4* 21 -32	5* 13 32	-1 98 76	3* 45 -41	8 83 -81	8 231 228	5 341 365
0 89 96	-3 66 93	6 64 63	0 136-120	4* 18 -37	9 152 160	9 117-114	6 110-101
1* 0 0	-2 96 -82	7 72 -79	1* 51 48	5* 18 18	10* 48 -68	10 57 62	7* 42 57
2* 0 -13	-1 130-151	8 65 -59	2 53 33	6 80 77	11* 46 29	11 135-119	8 222-216
3 66 -55	0 110 98	9 99 88	3 55 -53	7* 47 -55	K,L= -2 4	12 79 92	9 214 192
4* 0 6	1* 39 15	K,L= 2 3	K,L= 6 3	8* 51 44	-12 63 -53	K,L= 1 4	10 151-136
5* 0 13	2 100-107	-11 64 -69	-8* 43 -52	K,L= -5 4	-11* 31 37	-13* 41 46	11 150 136
6* 0 26	3 156 176	-10 88 88	-5 82 59	-10* 34 49	-10* 0 0	-12 69 -84	K,L= 4 4
7* 43 -41	4 78 -57	-9* 16 19	-4* 0 21	-9 125-133	-9* 0 -1	-11* 23 53	-10 96 108
K,L= -5 3	5* 0 37	-8* 15 -29	-3 67 -62	-8 121 151	-8* 0 -24	-10* 0 -16	-9 118-145
-10* 41 42	6* 43 35	-7* 0 19	-2 80 -64	-7 107-112	-7 75 65	-9* 0 3	-8* 26 66
-9* 0 -17	7 114-121	-6* 18 -41	-1 97 95	-6 130 142	-6 92 -93	-8* 0 -8	-7* 26 -47
-8* 38 -40	8* 0 -23	-5* 12 -33	0* 0 -7	-5 174-186	-5 141 129	-7* 34 52	-6 133 123
-7* 0 -15	9 105 102	-4 152 146	K,L= 8 3	-4 188 195	-4 175-157	-6* 31 -61	-5 65 -72
-6 82 63	K,L= -1 3	-3 278-236	1 82 22	-3 193-204	-3 206 180	-5* 0 25	-4* 0 9
-5* 0 2	-11* 52 -46	-2 52 32	K,L= -9 4	-2 256 237	-2 209-215	-4* 12 -17	-3 83 -58
-4* 47 -37	-10 78 69	-1 230 183	-4 58 -51	-1 266-258	-1 219 197	-3 126 92	-2 67 49
-3* 0 10	-9* 45 -32	0* 42 -29	-3 62 55	0 288 291	0 158-150	-2* 25 -36	-1 184-152
-2* 39 37	-8* 0 -18	1* 0 12	-2* 29 -34	1 338-332	1 175 157	-1 239-228	0 200 167
-1 66 -54	-7 72 52	2 68 53	-1* 0 -2	2 272 257	2 303-287	0 128 127	1 164 77
0 96 75	-6* 0 22	3 154-136	0* 51 49	3 208-217	3 296 306	1* 8 13	2* 0 -16
1 117 -94	-5* 31 -32	4* 33 -29	1 55 -45	4 245 246	4 201-206	2 181 178	3 84 -80
2* 0 -17	-4* 37 56	5* 52 31	2* 0 -1	5 171-167	5 274 309	3 92 -69	4 152-140
3 88 65	-3 327-340	6* 0 -10	3* 27 29	6 143 154	6 255-265	4 61 -36	5 125 120
4* 0 -28	-2 226 195	7 56 49	K,L= -8 4	7 187-208	7* 0 48	5 132-110	6 120 109
5* 0 9	-1 218 203	8* 0 10	-7 83 90	8 194 196	8 121-109	6 178 141	7 69 -71
6 82 83	0* 0 -20	9* 0 9	-6 125-135	9 163-155	9 189 194	7 190-185	8 97 -97
7 62 -75	1 165-167	10* 51 -43	-5 141 163	10 74 68	10 130-140	8 204 186	9 77 74
K,L= -4 3	2 151 170	K,L= 3 3	-4 112-114	K,L= -4 4	11 132 128	9* 25 -47	K,L= 5 4
-12* 37 -34	3 117-134	-10* 0 -17	-3 131 147	-11 100 100	K,L= -1 4	10* 0 38	-11 69 -76
-10* 0 13	4 121 118	-9* 46 38	-2 184-210	-10 134-148	-10 59 66	11 112-105	-10 101 122
-8 72 -65	5 124-107	-8* 0 -24	-1 137 153	-9* 0 -24	-9 112-111	K,L= 2 4	-9 126-160
-7 78 80	6* 0 -9	-6* 28 -32	0 111-120	-8 72 56	-8 207 207	-12 90-113	-8 142 181
-6 89 -84	7* 35 -30	-5* 50 46	1 141 158	-7 106 100	-7 181-172	-11 171 202	-7 176-208
-5 118 109	8 122 110	-4* 34 4	2 134-152	-6* 0 -18	-6 85 66	-10 118-130	-6 201 218
-4 54 -56	9* 45 -46	-3 65 58	3 115 122	-5 70 -51	-5 177-162	-9 93 92	-5 214-225
-3* 25 -22	10* 0 28	-2 56 -40	4 140-135	-4 152-135	-4 155 131	-8 171-167	-4 239 231
-2 59 -43	11* 38 -21	-1 132 114	5 131 138	-3 132 119	-3 103 84	-7 185 173	-3 296-250
-1 192 181	K,L= 0 3	0 179-159	6 103-112	-2* 0 -7	-2* 50 36	-6 207-181	-2 326 275
0 265-253	-12 52 35	1 61 -57	7 95 96	-1* 15 -28	-1 263-289	-5 265 260	-1 307-286
1 120 101	-10* 0 -35	2* 19 -19	K,L= -7 4	0 170 144	0 159 170	-4 366-334	0 352 353
2* 23 23	-9* 0 7	3 87 78	-8* 27 30	1 109 -80	1* 10 -5	-3 356 322	1 306-308

atom of water molecule could be located at approximately $z=1/4$, and two potassium ions at $z=0$ and 1/2, respectively.

Seven iterations of the block-diagonal least-squares refinement with isotropic thermal factors reduced the R value to 0.151. Then, anisotropic thermal factors were introduced, and the refinement was continued until all the parameter shifts became less than one tenth the estimated standard deviations. The final R value was 0.109 for nonzero reflections. A quantity $\sum w(|F_o|-|F_c|)^2$ was minimized, with $w=1.0$ if $F_o>5.0$ and $w=0.5$ otherwise. All the data including zero reflections were used in the calculation with the exception of the reflection 100, which seemed to be seriously suffering from secondary extinction effect. The atomic scattering factors for a potassium ion, neutral oxygen and carbon atoms were taken from Ref. 8. The final positional and thermal parameters are listed in Table 1. Numbering of atoms is shown in Fig. 1. The observed and calculated structure factors are given in Table 2.

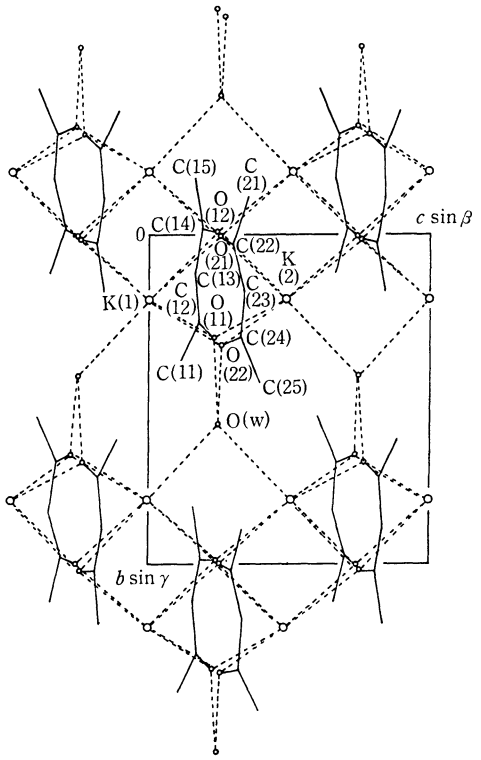

Fig. 1. Projection of the molecular skeleton along the a-axis. Solid lines indicate the acetylacetone framework and broken lines indicate the potassium-oxygen and oxygen-oxygen interactions. The numbering of the atoms refers to that in Table 1.

The space group assignment was finally checked by the distribution of the structure amplitudes.[9] The ratio of $\overline{F^2}/\overline{F}^2$ was found to be 0.631, while the theoretical values for centric and acentric distributions are 0.637 and 0.785, respectively. An $N(z)$ test[10] was also applied and indicated clearly the presence of a center of symmetry in agreement with the assigned space group.

Most of the calculations were carried out by using the UNICS programs[11] on a HITAC 8800 computer at the Computer Center of the University of Tokyo.

Results and Discussion

The crystal structure of PAH is shown in Fig. 1. Each potassium ion is surrounded by seven oxygen atoms, six of which belong to four different acetylacetone anions and the rest is a water molecule. The potassium-oxygen distances are in the range of 2.65 to 3.05 Å, as shown in Table 3.

The structures of several crystals including potassium ions in various coordination numbers were reported.

Table 3. Distances (d/Å) and angles (φ/°) with their estimated standard deviations shown in parentheses

The superscripts indicating the equivalent positions are shown at the right side of the bottom.

O(11)–C(12)	1.25(2)	C(12)–C(13)	1.44(2)	O(11)–C(12)–C(11)	121(2)
O(12)–C(14)	1.26(2)	C(13)–C(14)	1.40(2)	O(21)–C(22)–C(21)	118(1)
O(21)–C(22)	1.27(2)	C(22)–C(23)	1.40(2)	O(12)–C(14)–C(15)	116(2)
O(22)–C(24)	1.24(2)	C(23)–C(24)	1.40(2)	O(22)–C(24)–C(25)	119(2)
				C(12)–C(13)–C(14)	127(2)
C(11)–C(12)	1.52(3)	O(11)–O(12)	2.91(2)	C(22)–C(23)–C(24)	126(2)
C(14)–C(15)	1.53(3)	O(21)–O(22)	2.88(2)	C(11)–C(12)–C(13)	116(2)
C(21)–C(22)	1.50(3)	O(11)–O(22)	3.39(2)	C(21)–C(22)–C(23)	117(2)
C(24)–C(25)	1.53(3)	O(12)–O(21)	2.92(2)	C(13)–C(14)–C(15)	118(2)
				C(23)–C(24)–C(25)	115(2)
K(1)–O(11)	2.76(1)	K(2)–O(11)	2.75(1)	O(11)–C(12)–C(13)	124(2)
K(1)–O(12)	2.93(1)	K(2)–O(12)	2.77(1)	O(21)–C(22)–C(23)	125(2)
K(1)–O(21)	2.88(1)	K(2)–O(21)	3.05(1)	O(12)–C(14)–C(13)	126(2)
K(1)–O(22)	2.65(1)	K(2)–O(22)	2.74(1)	O(22)–C(24)–C(23)	126(2)
K(1)–O(12^{i})	3.01(1)	K(2)–O(12^{ii})	2.85(1)		
K(1)–O(21^{i})	2.81(1)	K(2)–O(21^{ii})	2.98(1)	none	x, y, z
K(1)–O(w^{iii})	2.83(1)	K(2)–O(w^{iv})	2.77(1)	i	$1-x$, $-y$, $-z$
				ii	$1-x$, $-y$, $1-z$
O(w)–O(11)	2.82(1)	K(1)–K(1^{i})	3.388(7)	iii	$1-x$, $1-y$, $-z$
O(w)–O(22)	2.72(1)	K(1)–K(2)	3.622(5)	iv	$1-x$, $1-y$, $1-z$
O(w)–K(1^{iii})	2.83(1)	K(2)–K(2^{ii})	3.403(7)	v	x, $-1+y$, z
O(w)–K(2^{iv})	2.77(1)				

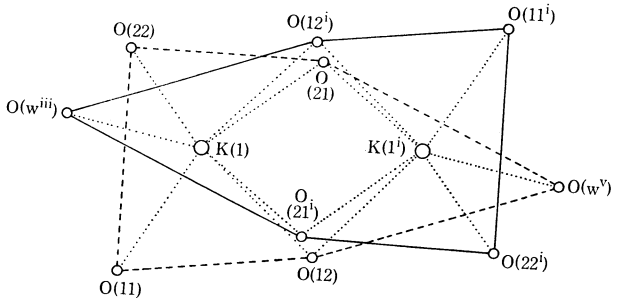

Fig. 2. Two distorted pentagons sandwiching two potassium ions.
The pentagons are shown by the solid and broken lines. The potassium ion interacts with seven oxygen atoms, as shown by dotted lines.

In potassium hydrogen bis(homophthalate),[12] the potassium ion is surrounded by four oxygen atoms at 2.76—2.80 Å. In potassium hexaiodatogermanate (IV),[13] there are two potassium ions in a tube of 18 oxygen atoms and each potassium ion is surrounded by nine oxygen atoms at 2.70—2.98 Å. In potassium hydrogen methylsuccinate,[14] the potassium ion is surrounded by a distorted tetrahedron of oxygen atoms at 2.705 to 2.763 Å and also by four oxygen atoms at longer distances of 2.956—3.085 Å. The observed K–O lengths for PAH are reasonable in comparison with these values.

The irregular seven-fold coordination of PAH can also be described, as a sandwich of two K^+ ions between two distorted pentagons shown in Fig. 2. The equation of the pentagonal plane through O(11), O(12), O(21), O(22) and O(w^{v}) is given in Table 4. The distance between the pentagonal plane is 3.7 Å. There is the crystallographically independent K^+ ion pair K(2)-K(2^{ii}), which takes the same arrangement as the K(1)-K(1^{i}) shown in Fig. 2. The distance of their pairs is about 3.4 Å.

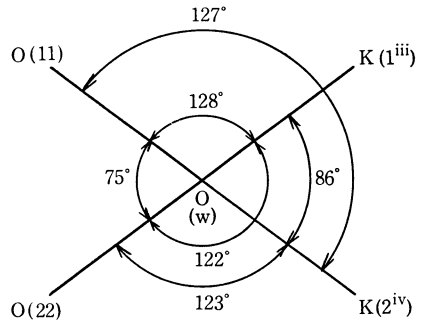

Fig. 3. Distorted tetrahedral environment of the water molecule.

The distorted tetrahedral environment of the water molecule consists of two K^+ ions and two oxygen atoms, as shown in Fig. 3. The distances of the OH···O hydrogen bonds are 2.82 and 2.72 Å. The mean values of intermolecular methyl–methyl and methyl–methylene carbon distances are 4.0 and 3.8 Å, respectively.

The mean values of bond lengths and angles in the acetylacetone anion are shown in Fig. 4. They are nearly equal to the corresponding mean values in heavy metal chelates of acetylacetone, as shown in

Table 4. Equations of the least-squares planes and the deviations of atoms from the planes [in square brackets] (d/Å)[a]

A) Planes of the acetylacetone skeleton OCCCO
$-0.3141\,u+0.0046\,v+0.9494\,w-0.5497=0$
[O(11), 0.009; O(12), −0.007; C(11), −0.123; C(12), −0.010; C(13), 0.000; C(14), 0.008; C(15), −0.012]
$0.3433\,u+0.0382\,v-0.9384\,w-0.5664=0$
[O(21), −0.022; O(22), 0.007; C(21), 0.021; C(22), 0.024; C(23), −0.004; C(24), −0.007; C(25), −0.181]

B) Pentagonal oxygen plane
$-0.0484\,u+0.0009\,v+0.9988\,w-1.5947=0$
[O(11), −0.059; O(12), 0.054; O(21), −0.050; O(22), 0.052; O(w^{v}), −0.005; K(1), −1.792; K(2), 1.824; K(1^{i}), 1.923; K(2^{ii}), 1.899]

a) u, v, and w are the orthogonal coordinates (Å) defined by $u=ax\sin\gamma+cz(\cos\beta-\cos\alpha\cos\gamma)/\sin\gamma$, $v=ax\cos\gamma+by+cz\cos\alpha$, $w=czE/\sin\gamma$, $E=(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma)^{1/2}$.

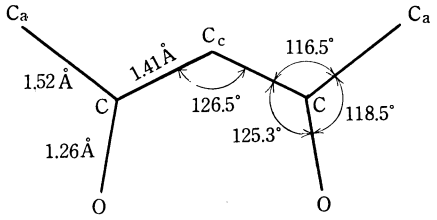

Fig. 4. Mean values of bond lengths and angles in an acetylacetone anion in PAH.

Table 5. Comparison of some parameters of acetylacetone groups

	PAH[a]	M(acac)$_n$[1]	acac[14]
C=O	1.26 Å	1.28 Å	1.315 Å
C–C$_c$	1.41	1.40	1.416
C–C$_a$	1.52	1.52	1.497
O···O	2.90	2.7—3.0	2.381
OCC$_c$	125.3°	125.3°	120.0°
OCC$_a$	118.5	115.7	120.0
CC$_c$C	126.5	124.5	118.0

a) Present study.

Table 5. The skeleton of the acetylacetone anion in PAH is also nearly planar (Table 4) because of π-electron delocalization, though the methyl carbon atoms [C(11) and C(25)] are significantly out of the plane as seen in the case of the heavy metal chelates. These facts seem to suggest, though not conclusive, that the bonding between the ligand and metal atoms in heavy metal chelates of acetylacetone is rather ionic as in PAH.

Recently the molecular structure of acetylacetone was determined by gas electron diffraction.[15] It is of interest to note that the structure of the enol form, as shown in Table 5, is considerably different from the structure of acetylacetone in both PAH and the heavy metal chelates, where a heavy metal atom replaces the hydrogen atom. The greater C=O distance and the smaller CC$_c$C angle in the enolic acetylacetone can be

attributed to strong interaction between the oxygen and the hydrogen atoms by the intramolecular hydrogen bond and thus to π-electron delocalization through the six-membered ring.

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