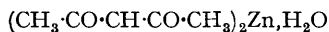


968. *The Stereochemistry of Acetylacetonone Complexes of Zinc. Part I.
The Crystal Structure of Monoaquobisacetylacetononezinc.*

By E. L. LIPPERT and MARY R. TRUTER.

One of the complexes obtained from an aqueous suspension of zinc hydroxide and acetylacetonone has a composition corresponding to



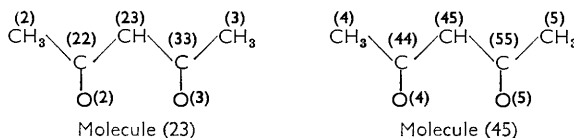
A three-dimensional *X*-ray crystal-structure analysis of this compound has shown that the zinc atom is 5-co-ordinated, with the bonds arranged in a trigonal bipyramid. The water molecule and one oxygen atom from each acetylacetonone group lie in the equatorial plane; the bond lengths are $\text{Zn}-\text{H}_2\text{O} = 2.02 \pm 0.03 \text{ \AA}$ and $\text{Zn}-\text{O} = 1.96 \pm 0.02 \text{ \AA}$. The other oxygen atoms of the chelating acetylacetonone groups form the apices of the bipyramid and the $\text{Zn}-\text{O}$ bond length is $2.11 \pm 0.02 \text{ \AA}$.

THE preparation of anhydrous acetylacetononezinc, as described by Morgan and Moss,¹ is extremely simple. The calculated amount of acetylacetonone is added to a hot aqueous suspension of zinc hydroxide, the suspension clears, and as the solution cools crystals of the complex separate. We have repeated this preparation and found that the system is more complicated. Usually we obtained colourless, needle-shaped crystals, type *A*, which on chemical analysis proved to be the monohydrate of acetylacetononezinc. Although the crystals were stable in air, they decomposed after a few days in the *X*-ray beam. Some preparations produced less stable, plate-like crystals, type *B*, which decomposed in a few days in the air and after only a few hours in the *X*-ray beam; preliminary measurements which are not altogether satisfactory indicate that this compound is probably diaquobis-acetylacetononezinc.

This paper describes the crystal structure analysis of the crystals of type *A*; for each

¹ Morgan and Moss, *J.*, 1914, **105**, 189.

zinc atom, there is one water molecule [which we designated O(1)] and two acetylacetonone groups which we numbered as shown:



METHODS AND RESULTS

Crystal Data.— $C_{10}H_{16}O_5Zn$, $M = 281.62$, m. p. 131° . Monoclinic, $a = 10.91 \pm 0.01$, $b = 5.517 \pm 0.005$, $c = 10.46 \pm 0.01$ Å, $\beta = 93.6^\circ \pm 0.2^\circ$, $U = 628$ Å³, $D_m = 1.50$ (by flotation), $Z = 2$, $D_c = 1.49$, $F(000) = 292$. Space group, $P2_1$ (C_2^2 , No. 4) established after structure analysis. Cu- K_α radiation, single-crystal oscillation and Weissenberg photographs, absorption coefficient, $\mu = 29.5$ cm⁻¹.

Structure Determination.—From the systematic absences, $(0k0)$ with k odd, the space group is not unambiguously determined and may be $P2_1$ or $P2_1/m$. There are two units of $Zn(C_5H_7O_2)_2 \cdot H_2O$ per unit cell, which means that all the atoms of one formula unit must be found if the space group is $P2_1$, while if the space group is $P2_1/m$ the zinc atom (and the water molecule) must lie either on a centre of symmetry, *e.g.*, at $0, 0, 0$, or in the mirror plane at $y = \frac{1}{2}$. Statistical tests are unlikely to provide a reliable differentiation because the scattering power of one of the atoms is much greater than that of the others.^{2,3}

A Patterson projection along $[010]$ showed that the zinc atom did not lie on a centre of symmetry and gave the x and z co-ordinates for this atom. Successive Fourier syntheses and difference Fourier syntheses served to locate all the carbon and oxygen atoms. The projection is well resolved as shown in Fig. 1; as every atom in the acetylacetonone groups appears, none of them can be related by the mirror plane, and the groups appear too distorted to be lying in the mirror plane parallel to (010) . Hence, the space group is $P2_1$.

For the $[001]$ projection, the x co-ordinate for zinc was taken as that determined from the $[010]$ projection, and the y co-ordinate was taken as 0.250 (any value for y may be chosen for one atom in the space group $P2_1$). Structure factors were calculated for this atom only (and so corresponded to a structure with a mirror plane at $y = 0.250$) and a Fourier synthesis was carried out; the resulting electron-density projection was difficult to interpret because each atom appeared on both sides of a mirror plane at $y = 0.250$; the method of solving this problem has been described for the more complicated case of cholesteryl iodide,⁴ so we give no details here. With the aid of the known x co-ordinates we were able, after several successive structure-factor calculations and Fourier syntheses, to locate the five oxygen atoms and four of the carbon atoms.

We had been unable to locate six of the carbon atoms by two-dimensional methods, so we calculated three-dimensional structure factors from the known co-ordinates of the zinc atom and nine light atoms; at this stage the agreement index, R , was 0.23 ($R = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}$). A three-dimensional Fourier difference synthesis gave the difference between the observed and the calculated electron densities throughout the unit cell; six positive peaks appeared in positions which, with the atoms already known, showed a recognisable structure as depicted in projection in Figs. 1 and 2. A view of the molecule along $[001]$ shows (Fig. 3) why we were unable to solve this projection.

Three-dimensional refinement of the co-ordinates of the atoms other than hydrogen was carried out by the method of least squares, and the individual anisotropic thermal motion parameters for each atom were determined. The value of R was reduced to 0.12 . The observed structure amplitudes and the real and the imaginary parts of the calculated structure factors are given in Table 1. From the final parameters a set of structure factors was also calculated for the reflections that were too weak to be observed; the value of R was 0.09 with $|F_o|$ taken as half the minimum observable.

² Hargreaves, *Acta Cryst.*, 1955, **8**, 12.

³ Truter, Cruickshank, and Jeffrey, *Acta Cryst.*, in the press.

⁴ Carlisle and Crowfoot, *Proc. Roy. Soc.*, 1945, *A*, **184**, 64.

FIG. 1. Projection of the structure along [010]. The molecule shown by full lines corresponds to the co-ordinates in Table 2; application of the two-fold screw axis (giving the co-ordinates $-x|a, \frac{1}{2} + y|b, -z|c$) produces the molecule shown by broken lines.

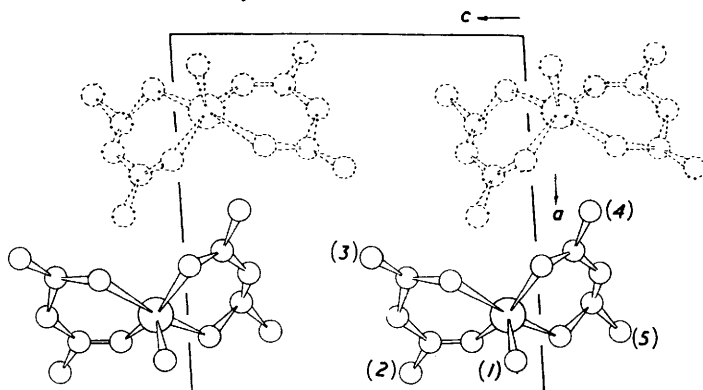


FIG. 2. Projection of the structure along [100]. Full and broken lines have the same significance as in Fig. 1. The dotted line indicates the hydrogen bond, 2.95 Å, from the water molecule in one complex to O(2') in another; the other hydrogen bond, 2.67 Å, to O(5'') lies nearly parallel to the [100] axis.

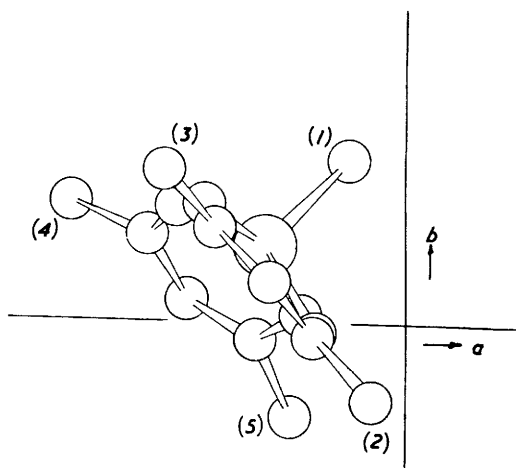
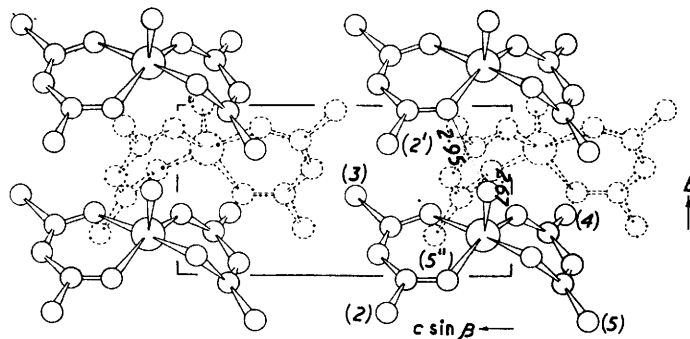


FIG. 3. One molecule seen in projection along [001].

Finally, the structure determination was checked by a complete three-dimensional Fourier difference synthesis. No positive value of the electron-density difference greater than 1 electron \AA^{-3} was found. It was not possible to identify the peaks as hydrogen atoms.

TABLE I. (Continued.)

<i>l</i>	$ F_o $	$ F_c \cos \alpha$	$ F_c \sin \alpha$	$ F_o $	$ F_c \cos \alpha$	$ F_c \sin \alpha$	<i>l</i>	$ F_o $	$ F_c \cos \alpha$	$ F_c \sin \alpha$	$ F_o $	$ F_c \cos \alpha$	$ F_c \sin \alpha$		
54 <i>l</i>			74 <i>l</i>			10,1, <i>l</i>			-10 <i>l</i>						
0	219	193	-115	0	86	-93	27	0	147	123	-65	1	244	-383	0
1	158	223	40	80 <i>l</i>			0	3	115	-108	55	2	123	41	0
2	136	94	22	1	90	-87	0	4	124	-115	6	3	253	-244	0
60 <i>l</i>			80 <i>l</i>			10,2, <i>l</i>			-11 <i>l</i>						
0	122	100	0	2	208	-228	0	5	121	-118	-9	4	370	-390	0
1	57	-35	0	3	333	-341	0	6	139	-143	-20	5	218	-187	0
3	333	368	0	4	204	-197	0	8	43	10	31	6	121	-100	0
4	370	368	0	5	134	-133	0	9	30	29	-11	7	60	57	0
5	273	306	0	6	143	179	0	10,3, <i>l</i>			-12 <i>l</i>				
6	76	58	0	7	205	209	0	0	122	-123	31	10	123	198	0
7	139	-125	0	8	100	98	0	1	141	-145	20	-11 <i>l</i>			
8	148	-152	0	9	136	145	0	2	165	-169	44	1	466	-539	203
9	161	-160	0	10	65	69	0	3	117	-87	42	2	528	-620	-361
10	97	-117	0	11	74	34	0	7	94	100	9	3	324	-178	-269
12	67	-21	0	81 <i>l</i>			8	69	89	10	4	417	208	-319	0
61 <i>l</i>			82 <i>l</i>			11,0, <i>l</i>			-12 <i>l</i>						
0	302	294	62	0	251	-212	-78	0	104	-110	0	1	441	354	229
1	323	336	54	1	105	-92	-6	2	90	103	0	2	375	328	91
2	330	311	83	2	65	-43	-59	3	114	127	0	3	489	429	-180
4	128	-94	72	3	137	16	-118	4	121	135	0	4	305	268	-8
5	260	-222	-30	4	113	85	-50	5	95	91	0	7	188	-173	-13
6	210	-166	65	5	147	131	17	6	83	82	0	8	198	-177	8
8	91	-49	-41	6	153	134	53	7	51	27	0	9	120	-123	7
9	65	20	34	7	92	49	66	11,1, <i>l</i>			-13 <i>l</i>				
10	119	99	27	8	120	-108	5	0	123	116	15	10	141	-130	-17
11	78	66	16	9	97	-94	-1	1	78	71	-4	11	70	-72	19
62 <i>l</i>			83 <i>l</i>			11,2, <i>l</i>			-14 <i>l</i>						
0	163	106	-21	0	141	148	-74	2	89	91	-6	2	290	228	-147
1	161	-110	109	1	177	152	-1	3	74	58	-29	3	98	-29	-108
2	240	-197	41	4	99	-80	36	6	89	-98	-2	4	369	-205	-54
3	239	-201	-6	5	177	-152	38	7	78	-87	-32	5	263	-219	38
4	239	-174	-33	6	152	-123	85	0	68	71	39	6	271	-195	42
5	80	-50	7	7	105	-80	67	3	63	-57	17	7	228	-170	98
8	106	84	19	0	113	122	0	4	109	-102	-2	8	177	-105	96
9	144	159	-17	1	100	89	0	5	97	-110	-3	10	85	84	57
10	102	98	-20	4	176	-176	0	6	69	-75	-7	-15 <i>l</i>			
63 <i>l</i>			90 <i>l</i>			11,3, <i>l</i>			-16 <i>l</i>						
0	203	-148	150	5	148	-176	0	0	99	-103	39	1	518	-638	0
1	195	-193	-25	6	134	-132	0	1	120	-100	5	2	299	-350	0
2	98	-95	-59	10	99	103	0	2	92	-95	38	3	324	-288	0
5	225	168	-10	91 <i>l</i>			12,0, <i>l</i>			-20 <i>l</i>					
6	233	226	-77	0	131	-109	-69	0	64	-68	0	1	344	-46	0
7	163	143	-116	1	139	-116	-61	1	70	-50	0	5	300	289	0
8	92	74	-81	2	165	-142	25	2	57	58	-19	6	231	261	0
70 <i>l</i>			92 <i>l</i>			12,1, <i>l</i>			-21 <i>l</i>						
0	332	-302	0	3	169	-165	42	3	91	105	-30	7	183	175	0
1	258	-244	0	4	89	-32	67	4	68	85	-18	8	85	91	0
2	292	-296	0	5	106	33	59	5	61	82	0	9	110	102	0
4	132	119	0	6	110	115	31	6	48	64	-4	10	65	-76	0
5	83	73	0	7	146	140	38	12,2, <i>l</i>			-22 <i>l</i>				
6	86	100	0	8	78	79	44	0	85	95	-1	11	108	-112	0
10	60	-87	0	9	78	86	29	1	113	107	12	12	104	-129	0
11	74	-82	0	10	80	31	20	2	80	96	-3	13	57	-82	0
71 <i>l</i>			93 <i>l</i>			12,3, <i>l</i>			-23 <i>l</i>						
0	75	-29	-70	0	111	-78	29	0	60	54	70	1	451	489	116
1	84	52	-29	1	85	-82	-15	1	85	-43	5	2	196	131	155
2	258	209	-57	2	106	-112	-31	2	85	-89	12	3	368	424	-13
3	272	258	-25	3	85	4	-88	3	85	-89	12	4	351	365	27
4	228	209	-25	4	85	22	-39	5	252	210	-10	5	252	210	-10
5	135	117	-33	5	129	137	27	6	125	108	24	6	125	108	24
6	106	-73	-13	6	120	128	5	7	173	-162	7	7	173	-162	7
7	162	-106	85	7	69	73	-25	8	68	-86	16	8	68	-86	16
8	171	-151	-6	8	111	-78	29	0	56	56	0	9	113	-88	53
9	179	-182	-11	9	152	111	-98	4	51	-55	0	10	124	-105	-14
10	72	-67	-2	10	212	200	-79	5	46	-52	0	-24 <i>l</i>			
72 <i>l</i>			10,0, <i>l</i>			13,1, <i>l</i>			-25 <i>l</i>						
0	232	222	-33	0	91	78	0	0	78	-73	12	1	218	219	-104
1	167	163	-8	1	116	122	0	1	78	-81	-15	2	297	244	-54
4	170	-127	64	2	78	89	0	2	43	-50	-21	3	396	367	22
5	200	-143	23	3	100	-124	0	13,2, <i>l</i>			-26 <i>l</i>				
6	202	-171	59	4	155	162	-29	1	49	38	-19	4	217	30	112
7	162	-116	46	5	92	71	30	2	74	72	0	5	219	-184	-54
8	80	-54	19	6	100	-124	0	6	394	-357	-4	6	256	-240	122
10	97	94	-1	7	106	-113	0	7	286	-240	122	7	286	-240	122
73 <i>l</i>			10,1, <i>l</i>			13,2, <i>l</i>			-27 <i>l</i>						
0	139	106	-3	8	56	-49	0	8	85	-32	112	8	85	68	52
1	109	-2	135	9	51	-47	0	9	85	68	52	9	85	68	52
2	287	-252	78	10,0, <i>l</i>			13,1, <i>l</i>			-28 <i>l</i>					
3	167	-163	30	0	91	78	0	0	78	-73	12	2	297	244	-54
4	163	-138	-74	1	116	122	0	1	78	-81	-15	3	396	367	22
5	98	-61	5	2	78	89	0	2	43	-50	-21	4	217	30	112
7	92	79	47	3	100	-124	0	13,2, <i>l</i>			-29 <i>l</i>				
8	92	114	5	4	106	-113	0	1	49	38	-19	6	394	-357	-4
9	77	82	-1	5	8	56	-49	0	74	72	0	7	286	-240	122
				6	8	56	-49	0				8	85	-32	112
				7	51	-47	0					9	85	68	52

TABLE I. (Continued.)

<i>l</i>	$ F_o $	$ F_c \cos \alpha$	$ F_c \sin \alpha$	<i>l</i>	$ F_o $	$ F_c \cos \alpha$	$ F_c \sin \alpha$	<i>l</i>	$ F_o $	$ F_c \cos \alpha$	$ F_c \sin \alpha$	<i>l</i>	$ F_o $	$ F_c \cos \alpha$	$ F_c \sin \alpha$	
-23 <i>l</i>			-42 <i>l</i>			-62 <i>l</i>			-90 <i>l</i>							
1	136	-33	-163	1	260	-213	106	1	305	225	-95	1	212	185	0	
2	225	-226	-58	2	446	-439	46	2	268	251	-6	2	132	134	0	
3	386	-356	-17	3	373	-352	109	3	222	173	-97	3	81	76	0	
4	286	-216	62	4	194	-160	92	4	117	90	-86	7	67	-88	0	
5	177	-147	61	6	194	186	40	6	129	-36	-39					
7	98	95	61	7	236	225	-69	9	109	-106	28					
8	173	174	-46	8	202	159	-6				-91 <i>l</i>					
9	167	109	-20	9	116	82	-8				1	106	-67	-4		
10	148	136	-42	-43 <i>l</i>			-63 <i>l</i>			2	213	-170	-95			
-24 <i>l</i>			-44 <i>l</i>			-64 <i>l</i>			-92 <i>l</i>							
1	401	-375	85	1	270	-155	-47	1	369	262	22	3	185	-200	43	
2	201	-184	22	2	122	126	23	2	106	60	-37	4	162	-171	26	
3	217	3	42	3	360	245	125	3	169	-84	-81	5	81	-66	44	
-30 <i>l</i>			-50 <i>l</i>			-70 <i>l</i>			-93 <i>l</i>							
1	276	-243	0	1	106	95	0	1	277	-259	0	3	139	128	50	
2	216	229	0	2	51	47	0	2	189	-175	0	4	143	120	-51	
3	358	398	0	3	393	-347	0	3	141	88	0	5	86	62	-61	
4	486	472	0	4	370	-381	0	4	185	173	0	-10,0, <i>J</i>				
5	277	302	0	5	309	-321	0	5	189	200	0	2	70	-69	0	
6	143	136	0	6	270	-269	0	6	148	157	0	3	89	-105	0	
7	74	-63	0	9	92	100	0	7	72	99	0	4	134	-165	0	
9	85	-77	0	10	97	120	0	-71 <i>l</i>			5	114	-119	0		
10	81	-66	0	-51 <i>l</i>			-71 <i>l</i>			6	81	-89	0			
-31 <i>l</i>			-51 <i>l</i>			-71 <i>l</i>			-93 <i>l</i>							
1	437	243	-356	1	222	-197	-48	1	158	89	105	3	139	128	50	
2	294	263	-136	2	243	-239	83	2	251	236	86	4	143	120	-51	
3	378	344	176	3	245	-198	39	3	226	207	-51	5	117	121	-4	
4	290	-47	228	4	108	-54	114	4	134	125	-75	6	132	103	-4	
5	156	-68	70	5	97	76	123	5	92	22	-89	-10,1, <i>J</i>				
6	226	-215	38	6	159	162	84	6	94	-81	-67	1	173	-160	-3	
7	249	-257	-20	7	132	136	5	7	113	-112	8	6	61	66	17	
8	136	-140	54	8	126	132	73	8	113	-86	-68	7	54	67	-4	
9	92	-74	61	9	94	87	-17	-72 <i>l</i>			-10,2, <i>J</i>					
11	48	89	-13	-52 <i>l</i>			-72 <i>l</i>			-10,3, <i>J</i>						
-32 <i>l</i>			-52 <i>l</i>			-72 <i>l</i>			-10,3, <i>J</i>							
1	264	-218	-24	1	212	-135	-33	1	303	265	121	1	141	7	65	
2	358	-317	-156	2	130	-50	-73	2	176	95	57	3	129	118	20	
3	489	-450	-103	3	144	96	59	3	136	106	-56	4	126	99	-4	
4	302	-231	-109	4	139	158	36	5	146	-142	-15	5	123	114	-24	
5	242	-214	-52	5	173	203	29	6	159	-121	95	6	97	13	-32	
6	132	-93	115	6	184	184	-105	7	85	-91	28	-10,3, <i>J</i>				
8	211	199	-49	7	200	97	-65	-73 <i>l</i>			-10,3, <i>J</i>					
9	172	154	-38	8	85	-54	-41	-73 <i>l</i>			-10,3, <i>J</i>					
10	97	118	-30	9	80	-76	-15	-73 <i>l</i>			-10,3, <i>J</i>					
-33 <i>l</i>			-53 <i>l</i>			-73 <i>l</i>			-10,3, <i>J</i>							
1	432	-364	60	10	102	-104	17	1	214	-129	105	1	109	112	-37	
2	360	-332	94	11	57	-49	19	2	158	-178	-1	2	92	83	-70	
3	172	-128	131	-53 <i>l</i>			-73 <i>l</i>			3	85	31	-70			
4	109	-19	101	1	369	251	-183	3	111	-143	52	-11,0, <i>J</i>				
5	77	56	113	2	290	229	45	4	139	-96	71	1	134	-141	0	
6	193	130	62	3	121	108	-91	5	98	-35	54	3	49	-50	0	
7	238	199	-95	4	188	165	-48	6	98	82	38	4	41	24	0	
8	21	72	-24	6	139	-86	-62	7	109	94	6	-11,2, <i>J</i>				
9	92	39	-36	7	188	-180	78	8	86	92	-28	2	106	113	-68	
10	116	3	-66	-54 <i>l</i>			-80 <i>l</i>			-11,2, <i>J</i>						
-34 <i>l</i>			-54 <i>l</i>			-80 <i>l</i>			-11,2, <i>J</i>							
1	202	-172	109	1	221	107	-140	1	112	108	0	1	80	112	-5	
2	205	178	-25	3	210	-181	-40	2	250	292	0	2	106	113	-68	
3	190	145	-39	-55 <i>l</i>			-81 <i>l</i>			-11,3, <i>J</i>						
-35 <i>l</i>			-60 <i>l</i>			-81 <i>l</i>			-11,3, <i>J</i>							
1	217	231	-75	1	181	-206	-3	3	247	249	0	1	85	75	-75	
-40 <i>l</i>			-60 <i>l</i>			-81 <i>l</i>			-11,3, <i>J</i>							
1	37	-36	0	1	49	-20	0	4	207	196	0	-12,0, <i>J</i>				
2	201	167	0	2	247	-259	0	5	114	113	0	1	56	29	0	
3	165	133	0	3	352	-337	0	6	59	56	0	3	53	-7	0	
4	213	-207	0	6	121	122	0	7	92	-79	0	-12,1, <i>J</i>				
5	159	-147	0	7	116	123	0	8	89	-132	0	1	90	90	-48	
6	199	-210	0	8	95	108	0	-82 <i>l</i>			2	78	74	-46		
7	44	-41	0	9	89	87	0	1	264	256	134	4	69	18	-41	
8	46	-44	0	-61 <i>l</i>			-82 <i>l</i>			-12,3, <i>J</i>						
9	167	-160	0	1	303	-310	22	2	178	132	69	-13,0, <i>J</i>				
11	65	75	0	2	118	-98	40	4	65	-45	29	1	90	90	-48	
12	70	82	0	3	177	164	50	5	69	-58	-60	2	78	74	-46	
-41 <i>l</i>			-61 <i>l</i>			-82 <i>l</i>			-12,3, <i>J</i>							
1	172	-11	-187	4	187	182	-34	6	133	-114	7	4	69	18	-41	
2	43	1	-61	5	181	192	-38	7	115	-106	-32	-12,3, <i>J</i>				
3	336	-310	94	6	176	135	-96	8	61	-40	-4	1	185	-95	-8	
4	434	-483	40	7	117	110	6	-83 <i>l</i>			2	171	-70	11		
5	290	-290	156	8	69	49	3	1	185	-144	57	-13,0, <i>J</i>				
6	168	-140	101	9	90	-69	-59	2	143	-116	73	-13,0, <i>J</i>				
9	94	99	34	10	100	-125	-1	3	6	148	134	3	37	55	0	
10	119	110	-43							4	65	-45	29			

Results.—The final values of the atomic co-ordinates are given in Table 2 as fractions of the unit-cell edges, and in Å with respect to orthogonal axes parallel to the crystallographic a , b , and c^* axes for X' , Y' , and Z' respectively. Table 2 also shows σ , the estimated standard

TABLE 2. Atomic co-ordinates.

	x/a	y/b	z/c	$X' (\text{Å})$	$\sigma(X) (\text{Å})$	$Y' (\text{Å})$	$\sigma(Y) (\text{Å})$	$Z' (\text{Å})$	$\sigma(X) (\text{Å})$
Zn	0.7843	0.2417	0.0889	8.499	0.003	1.333	(0.009)	0.930	0.003
O(1)	0.912	0.505	0.076	9.899	0.016	2.784	0.025	0.789	0.018
O(2)	0.860	-0.025	0.196	9.252	0.020	-0.138	0.024	2.043	0.018
O(3)	0.691	0.363	0.249	7.373	0.018	2.002	0.023	2.602	0.019
O(4)	0.645	0.359	-0.015	7.051	0.017	1.983	0.024	-0.158	0.015
O(5)	0.845	0.025	-0.059	9.255	0.015	0.140	0.023	-0.618	0.015
C(2)	0.949	-0.231	0.373	10.11	0.03	-1.27	0.05	3.89	0.03
C(3)	0.630	0.475	0.469	6.57	0.03	2.62	0.05	4.89	0.03
C(4)	0.490	0.368	-0.165	5.46	0.03	2.03	0.04	-1.72	0.03
C(5)	0.827	-0.275	-0.232	9.18	0.03	-1.52	0.05	-2.42	0.03
C(22)	0.862	-0.030	0.324	9.19	0.03	-0.17	0.05	3.38	0.03
C(23)	0.791	0.125	0.403	8.37	0.03	0.69	0.04	4.21	0.03
C(33)	0.705	0.293	0.367	7.45	0.03	1.61	0.04	3.83	0.03
C(44)	0.604	0.276	-0.112	6.67	0.02	1.52	0.04	-1.17	0.02
C(45)	0.664	0.074	-0.186	7.37	0.02	0.41	0.04	-1.95	0.03
C(55)	0.773	-0.043	-0.155	8.53	0.03	-0.24	0.04	-1.62	0.03

deviations in the co-ordinates; these are actually minimum values because in their calculation it has been assumed that changes in co-ordinates of one atom do not affect those of the other atoms. This is not a valid assumption for a non-centrosymmetrical structure containing a heavy atom^{5,6} because small changes in the position of the heavy atom have a relatively large effect on the phase angles. This uncertainty applies particularly to the y co-ordinates because there is no fixed origin in this direction and atoms can be located only in relation to one another; it is best to choose the heaviest atom as the origin. In principle,⁵ the true values of the standard deviations can be calculated; for a very simple structure,⁶ sodium nitrite, calculation showed that the true standard deviations in the parameters of the oxygen and nitrogen atoms were double the apparent values. Unfortunately, this structure has too many parameters for the calculation to be possible even on the Ferranti Pegasus electronic computer.

Table 3 shows the thermal parameters, and their minimum standard deviations; U_{11} , U_{22} , and U_{33} are the mean square amplitudes of vibration parallel to the a^* , b^* , and c^* axes respectively and with U_{12} , U_{23} , and U_{13} give the magnitude and orientation of the ellipsoid of vibration with respect to the crystallographic axes.

TABLE 3. Thermal parameters (all units are 10^{-3}Å^2).

	U_{11}	σ	U_{22}	σ	U_{33}	σ	U_{12}	σ	U_{23}	σ	U_{13}	σ
Zn	38	1	14	2	36	1	-21	2	23	2	-8	1
O(1)	33	8	40	17	54	10	-9	10	-9	12	-7	7
O(2)	77	13	10	13	51	10	-5	12	25	11	-29	9
O(3)	48	9	10	12	59	11	-7	10	15	11	-2	8
O(4)	50	9	36	15	34	8	2	10	27	9	-24	7
O(5)	39	8	19	13	34	8	-0	10	12	10	-9	6
C(2)	67	17	42	30	70	17	22	23	-11	26	-27	14
C(3)	55	16	80	37	65	17	44	22	-49	24	-14	14
C(4)	57	16	20	22	63	17	-3	17	-16	18	-23	13
C(5)	70	17	49	25	56	14	45	26	-21	26	5	12
C(22)	54	15	72	35	44	14	-9	20	45	19	6	12
C(23)	66	17	50	25	35	12	50	18	1	15	-5	11
C(33)	55	14	66	39	62	15	-44	21	45	23	-30	12
C(44)	28	9	72	30	39	11	37	18	-28	21	4	8
C(45)	37	12	55	29	67	18	-29	17	36	21	-25	12
C(55)	80	20	10	19	57	16	25	19	-13	18	-13	15

In Table 4 the bond lengths and angles are given; the minimum standard deviations derived from those in Table 2 are, for the bond lengths: Zn-O \pm 0.02 Å, O-C \pm 0.03 Å, C-C \pm 0.05 Å; and for the angles: O-Zn-O \pm 1°, Zn-O-C \pm 2°, O-C-C \pm 2.5°, C-C-C \pm 3°.

⁵ Cruickshank, *Acta Cryst.*, 1952, **5**, 511.

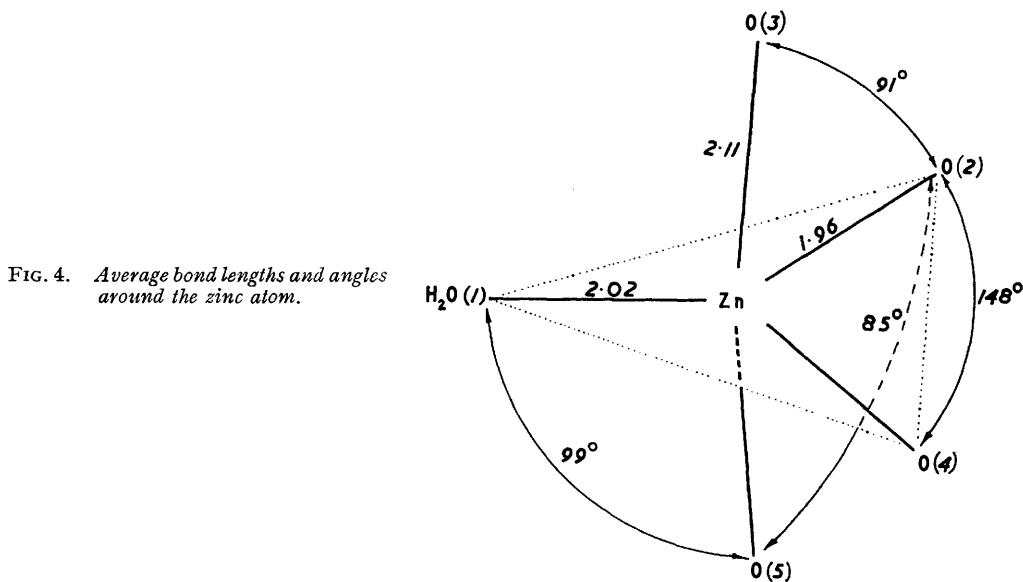
⁶ Truter, *Acta Cryst.*, 1954, **7**, 73.

TABLE 4. Bond lengths and angles.

Zn-O(1)	2.02 Å	O(1)-Zn-O(2)	108°	Zn-O(2)-C(22)	124°
Zn-O(2)	1.99	O(1)-Zn-O(4)	104	Zn-O(3)-C(33)	129
Zn-O(3)	2.13	O(1)-Zn-O(3)	101	Zn-O(4)-O(44)	127
Zn-O(4)	1.92	O(1)-Zn-O(5)	96	Zn-O(5)-C(55)	123
Zn-O(5)	2.09				
		O(2)-Zn-O(3)	90	O(2)-C(22)-C(2)	109
O(2)-C(22)	1.34	O(4)-Zn-O(5)	93	O(3)-C(33)-C(3)	113
O(3)-C(33)	1.29	O(2)-Zn-O(5)	82	O(4)-C(44)-C(4)	118
O(4)-C(44)	1.17	O(4)-Zn-O(3)	87	O(5)-C(55)-C(5)	113
O(5)-C(55)	1.29				
		O(2)-Zn-O(4)	148	O(2)-C(22)-C(23)	126
C(2)-C(22)	1.53	O(3)-Zn-O(5)	162	O(3)-C(33)-C(23)	121
C(3)-C(33)	1.71			O(4)-C(44)-C(45)	125
C(4)-C(44)	1.42			O(5)-C(55)-C(45)	122
C(5)-C(55)	1.65				
C(23)-C(22)	1.45			C(2)-C(22)-C(23)	126
C(23)-C(33)	1.35			C(3)-C(33)-C(23)	125
C(45)-C(44)	1.53			C(4)-C(44)-C(45)	117
C(45)-C(55)	1.37			C(5)-C(55)-C(45)	126
				C(44)-C(45)-C(55)	128
				C(22)-C(23)-C(33)	129

These have been calculated from the results given by the electronic computer to four decimal places, not from the rounded-off values in Table 2.

Another estimate of the uncertainties in the individual bond lengths is the average deviation from the arithmetic mean of the independently determined values for the same kind of bond, this gives: Zn-O \pm 0.03 Å, O-C \pm 0.05 Å, C-C \pm 0.08 Å. Similar treatment for the angles gives: O-Zn-O \pm 2°, Zn-O-C \pm 2.3°, O-C-C \pm 2.5°, C-C-C \pm 3.3°. The average bond



lengths and angles round the zinc atom are shown in Fig. 4. It can be seen that the arrangement is that of a distorted trigonal bipyramid. The equatorial plane is defined by the equation

$$0.390X' - 0.437Y' - 0.810Z' - 1.988 \text{ \AA} = 0$$

The acetylacetonone groups are planar (within ± 0.07 Å) and the zinc atom is not included in either plane, being 0.3 Å from that of the molecule (23) and 0.4 Å from that of molecule (45). The standard deviations in the bond lengths within the acetylacetonone groups are so large that

no deductions can be made from them except that, in so far as the average values (Fig. 5) are reasonable, they confirm the correctness of the structure analysis.

All the intermolecular contacts of less than 3.5 Å were calculated and only six were found. The two shortest are 2.95 Å and 2.67 Å, both from the water molecule to other oxygen atoms as shown in Fig. 2, suggesting that these are hydrogen bonds; the angles subtended at the water molecule are $\text{Zn-O}(1) \cdots \text{O}(2)'$ 117°, $\text{Zn-O}(1) \cdots \text{O}(5)''$ 136°, and $\text{O}(2)' \cdots \text{O}(1) \cdots \text{O}(5)''$ 102°, which are consistent with hydrogen bonds between the oxygen atoms. Of the other

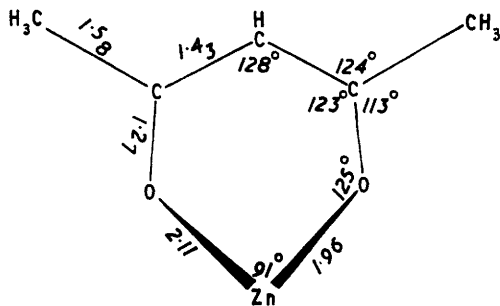


FIG. 5. Average bond lengths and angles in an acetylacetonate group.

van der Waals contacts $\text{O}(1) \cdots \text{O}(5)'$ [comparable to $\text{O}(1) \cdots \text{O}(2)'$] in Fig. 2 is 3.26 Å, which is too long for a hydrogen bond and not at a reasonable angle to the other bonds round $\text{O}(1)$, and the rest involve methyl groups, *viz.*, $\text{C}(4) \cdots \text{O}(3)$ 3.42 and 3.46 Å, and $\text{C}(2) \cdots \text{O}(1)$ 3.46 Å.

DISCUSSION

Our structure analysis has shown with certainty the stereochemistry of this five-co-ordinated complex of zinc. Although four- and six-co-ordinated zinc complexes are well known, this is only the second five-co-ordinated complex found; the first, dichloro-terpyridylzinc,⁷ is also a distorted trigonal bipyramid. Both compounds are probably derived from $4s4p^34d$ hybridisation in the zinc ion. Distortions from the ideal bond angles, shown diagrammatically in Fig. 6, are different for the two compounds, presumably because of the need to reduce the distortions within the organic ligands; thus for the terpyridyl complex the equatorial bonds are formed by the two chlorine atoms and the central nitrogen atom of the terpyridyl group, and the other two Zn-N bonds are bent away from the ideal positions normal to the equatorial plane towards the Zn-N bond as shown in Fig. 6. On the other hand, for the chelate groups in the acetylacetonate complex the distortion of the axial bonds is towards the bisector of the $\text{O}(2)-\text{Zn}-\text{O}(4)$ angle in the equatorial plane.

The striking feature is that this five-co-ordinated complex is apparently more stable than either the anhydrous form, which would probably be tetrahedral, or the dihydrate, which would be octahedral. It is noteworthy that when Cotton and Hanson⁸ examined the soft *X*-ray absorption edge of a zinc acetylacetonate complex, made by Morgan and Moss's procedure,¹ they found that the compound did not give the results characteristic for tetrahedral zinc complexes and they tentatively suggested that it might be square or octahedral.

Discussion of the chemical significance of the bond lengths must be based on a reasonable estimate of their reliability and it is better to overestimate the limits of error. The minimum standard deviations and the most probable errors (derived from the internal consistency) are given in the section "Results" and suggest that the statistical standard deviations in the individual bond lengths should be increased by a factor of about 1.6; *

* These increased values were used in calculating the standard deviations in the mean bond lengths.

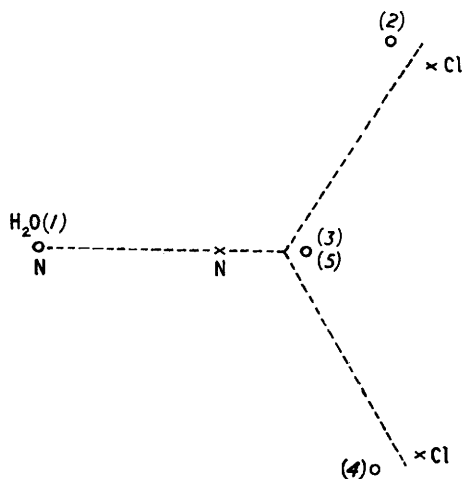
⁷ Corbridge and Cox, *J.*, 1956, 594.

⁸ Cotton and Hanson, *J. Chem. Phys.*, 1958, 28, 83.

the mean values for the Zn–O bonds are 2.11 ± 0.02 Å axial and 1.96 ± 0.02 Å equatorial (excluding the Zn–H₂O bond); this difference (0.15 Å) is definitely significant and is in the direction predicted theoretically⁹ for sp^3d hybridisation. The shorter bond length is the same as that found in compounds containing a tetrahedral arrangement of Zn–O bonds, 1.95 Å in zinc oxide,¹⁰ and 1.97 Å in zinc basic acetate.¹¹ The longer bond length appears comparable with the values for octahedrally co-ordinated zinc, but these differ considerably, being 2.17 and 2.18 Å in zinc acetate dihydrate¹² and 2.05 Å in the 8-hydroxyquinoline complex.¹³

Our Zn–H₂O bond length, 2.02 ± 0.03 Å, is not significantly greater than the corresponding Zn–O bond length (1.96 ± 0.02 Å). Other Zn–H₂O bonds are all in octahedral

FIG. 6. Diagram showing, in projection on the equatorial plane, the relation between an ideal trigonal bipyramid (broken lines), the distorted version in monoaquobisacetylacetonatezinc (circles represent the positions of the oxygen atoms) and in dichloropyridylzinc (crosses).



compounds and, as expected, are longer than this one; the values are 2.08 Å in the hexaquo-ion,¹⁴ 2.14 Å in zinc acetate dihydrate,¹² and 2.27 Å in the 8-hydroxyquinoline complex.¹³ For the last compound this represents a large difference between the Zn–O and Zn–H₂O bonds, similar to that established in bisacetylacetonatecobalt(II) dihydrate,¹⁵ whereas for the acetate the difference, though not significant, is in the opposite direction. Only more determinations can establish whether the bond lengths really vary from compound to compound, and perhaps provide an explanation if this is so.

EXPERIMENTAL

Preparation.—Morgan and Moss's procedure¹ was followed. Several preparations were made and care was taken that the crystals which were analysed and on which the density was determined were of the same batch as those used for X-ray work. The colourless acicular crystals (type *A*) were analysed (Found: C, 42.0; H, 5.2; Zn, 23.1. C₁₀H₁₆O₅Zn requires C, 42.7; H, 5.7; Zn, 23.2%) and found to correspond to monoaquobisacetylacetonatezinc. To prevent decomposition in the X-ray beam, the crystals used were kept in Lindemann glass tubes containing a few drops of acetylacetonate.

X-Ray Work.—Cu- K_{α} radiation was used. For type *B* crystals approximate unit-cell dimensions were obtained from single-crystal oscillation and Weissenberg photographs. For type *A* the dimensions of the *a* and *c* axes and the angle β were obtained by a least-squares

⁹ Kimball, *J. Chem. Phys.*, 1940, **8**, 188.

¹⁰ Bunn, *Proc. Phys. Soc.*, 1935, **47**, 835.

¹¹ Koyama and Saito, *Bull. Chem. Soc. Japan*, 1954, **72**, 112.

¹² Van Niekerk, Schoening, and Talbot, *Acta Cryst.*, 1953, **6**, 720.

¹³ Merrit, Cady, and Mundy, *Acta Cryst.*, 1954, **7**, 473.

¹⁴ Broomhead and Nicol, *Acta Cryst.*, 1948, **1**, 88.

¹⁵ Bullen, *Acta Cryst.*, 1959, **12**, 703.

procedure from the spacings measured for 15 reflections on a copper-calibrated Weissenberg photograph; the b axis was measured from (060) by the Straumanis method.

Equi-inclination Weissenberg photographs were taken about the b and c axes for all layer lines up to ($h3l$) and ($hk3$). Of the 1400 possible reflections, 841 gave measurable intensities, 200 were too weak to be observed, and 360 were inaccessible. A multiple-film technique was used; intensities were estimated visually by comparison with a calibrated strip and corrected for Lorentz and polarisation factors. For the ($h0l$) reflections, an approximately absolute scale was obtained by Wilson's method,¹⁶ and after the projection had been solved a more accurate value was obtained by making $\sum |F_o|$ equal to $\sum |F_c|$; this was used after correlation to put the three-dimensional values on the absolute scale. The correlation was carried out on the square roots of the corrected intensities by Dickerson's method.¹⁷

Very small crystals (maximum dimension 0.4 mm. parallel to b) were used and no absorption correction was applied.

Refinement Procedure.—The function minimised by least squares was $R' = \sum w (|F_o| - |F_c|)^2$, where the weighting factor, w , was $1/(4.2 + |F_o| + 0.0264|F_o|^2)$. The scattering factors were those of Berghuis *et al.*¹⁸ for oxygen, carbon, and zinc, the last being corrected for the real part of the anomalous dispersion;¹⁹ calculation showed that even in the most favourable examples the effect of the imaginary part of this correction was less than 10% in the intensity and thus within our error in estimation. The parameters were the scale factor, two co-ordinates for zinc, three co-ordinates for each of the carbon and oxygen atoms, and six for the thermal motion of each atom; the hydrogen atoms were neglected.

Computation.—One three-dimensional Fourier difference synthesis was carried out by Dr. O. S. Mills with his own programme on the London University Ferranti Mercury computer. The Leeds University Ferranti Pegasus computer was used for Fourier syntheses with a programme written by Dr. P. A. Samet, for least-squares refinement with programmes written by Dr. D. W. J. Cruickshank and Miss D. E. Pilling, and for interatomic distances and angles with a programme written by one of us (M. R. T.).

We are grateful to Professor E. G. Cox for his helpful advice. We thank the people who helped us with computation by carrying out the calculations or by letting us use their programmes, Dr. D. W. J. Cruickshank, Dr. O. S. Mills, Miss D. E. Pilling, Dr. P. A. Samet, and also the Director and staff of the Leeds University Computing Laboratory.

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¹⁶ Wilson, *Nature*, 1942, **150**, 152.

¹⁷ Dickerson, *Acta Cryst.*, 1959, **12**, 610.

¹⁸ Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

¹⁹ Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.