Acta Cryst. (1959). **12**, 703

The Crystal Structure of Cobalt(II) Bisacetylacetone Dihydrate

By G. J. Bullen*

Department of Chemical Crystallography, University College, Gower Street, London W. C. 1, *England*

(*Received* 26 *March* 1959)

Cobalt(II) bisacetylacetone dihydrate, $Co(C_5H_7O_2)_2.2H_2O$, is monoclinic,

$$a = 10{\cdot}91,\quad b = 5{\cdot}39,\quad c = 11{\cdot}19\ \text{Å};\quad \beta = 106{\cdot}0°,$$

space group $P2_1/c$, two centrosymmetric molecules in the unit cell. The atomic positions were determined by Fourier and least-squares refinement of X-ray diffraction data. The cobalt atom, lying on a centre of symmetry, is surrounded by four oxygen atoms of the acetylacetone chelate groups and two water molecules, forming a tetragonally distorted octahedron (Co–O 2·05, 2·06 Å; Co–H_2O 2·23 Å). The atoms of the acetylacetone group are very nearly coplanar but the cobalt atom lies 0·4 Å from their plane. The molecules are bound in layers by O · · · H–O hydrogen bonds of length 2·90–2·91 Å; between the layers are van der Waals forces.

Experimental

Crystals of cobalt(II) bisacetylacetone dihydrate suitable for X-ray examination were grown from a solution in dimethyl formamide. They are monoclinic prismatic, usually slightly elongated along *b*, with {100}, {001}, {$\bar{1}$02} and {011} well developed. There is moderate cleavage parallel to (100). The unit-cell dimensions, determined from Weissenberg photographs taken using Fe *K* radiation, are

$$a = 10{\cdot}91 \pm 0{\cdot}04,\quad b = 5{\cdot}39 \pm 0{\cdot}01,\quad c = 11{\cdot}19 \pm 0{\cdot}03\ \text{Å}\,,\quad \beta = 106{\cdot}0 \pm 0{\cdot}1°\,.$$

The observed density is 1·541 g.cm.$^{-3}$, calculated density for 2 molecules $Co(C_5H_7O_2)_2.2\,H_2O$ per unit cell 1·54±0·01 g.cm.$^{-3}$. The systematic absences of X-ray reflexions are: ($h0l$) absent when l is odd and ($0k0$) absent when k is odd, so that the space group is determined uniquely as $P2_1/c$. The red crystals show pronounced pleochroism, greatest when plane-polarized light is travelling perpendicular to (001). The crystals then appear deep red if the electric vector is parallel to the *a* axis, and light brown if it is parallel to *b*. The pleochroism is least when light is travelling perpendicular to (100). The direction of greatest absorption is *a*, medium *c*, and least *b*.

Intensities of ($h0l$), ($hk0$) and ($hk1$) reflexions were estimated visually from Weissenberg photographs taken using Mo*K* radiation. To obtain a range of intensity for each reflexion, instead of the usual method of interleaving films with metal foil, films of different speeds (Ilford Industrial *G* and *B*) were used (Iball, 1954). Reflexions were observed to a sin θ limit of 0·59. Roughly equidimensional crystals of side 0·3 mm. were used and, within this range of sin θ, absorption errors are negligible (linear absorption coefficient for Mo*K* radiation 14 cm.$^{-1}$). The cutting of crystals perpendicular to *b*, necessary for the ($hk0$) and ($hk1$) photographs, was liable to cause distortion of the crystal.

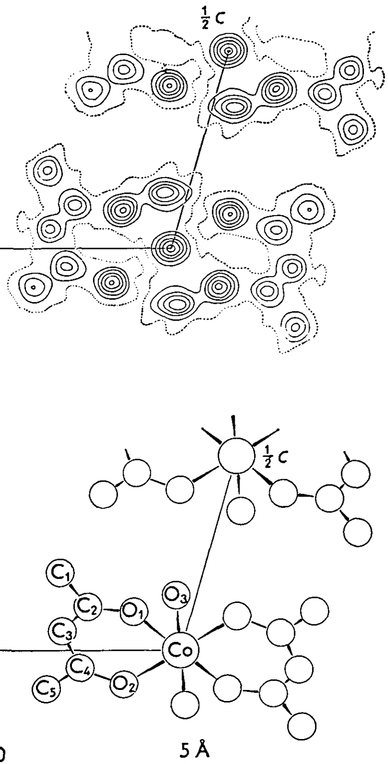


Fig. 1. Electron-density projection on (010). Contours at intervals of 2 e.Å^{-2} with the lowest contour at 2 e.Å^{-2} broken, except around the cobalt atom where the contours are at 2, 10, 20, 30, 40, 50 e.Å^{-2}.

---

* Present address: Birkbeck College Crystallography Laboratory, 21 Torrington Square, London W. C. 1, England.

Determination and refinement of the structure

Since the unit cell contains only 2 molecules in the space group $P2_1/c$, the Co atom must lie on a centre of symmetry. The carbon and oxygen atoms were located from a Fourier projection on (010) calculated using terms whose signs could be assumed to be fixed by the Co contribution. All atoms are fully resolved in this projection (Fig. 1) so that accurate x- and z-co-ordinates could be obtained. These co-ordinates were used, taking reasonable values for bond lengths, to assign approximate y-co-ordinates for the calculation of (hk0) structure factors and the (001) Fourier projection. In this projection there is poor resolution owing to overlap between molecules related by the glide plane, i.e. separated by $\frac{1}{2}c$. This difficulty can be overcome by using the (hk1) generalized projection, the cosine part of which is shown in Fig. 2. Here the overlapping atoms appear as peaks of opposite sign and are consequently resolved.

In refining the structure, hydrogen atoms were inserted at positions calculated to give C–H bond lengths of 1·09 Å,* and anisotropic temperature factors were applied to all atoms except hydrogen, for which an isotropic temperature factor, $B = 4{\cdot}2$ Å^2, was used. The orientation of each thermal ellipsoid (see Table 1) was chosen with reference to the environment of the atom (e.g. for C_1 the direction of minimum vibration is that of the C_1–C_2 bond), one axis of each ellipsoid being placed perpendicular to the mean plane of the cobalt–acetylacetone ring. The atomic co-ordinates and temperature factors for Co, O and C atoms were refined using a diagonal least-squares procedure. The orientations of the ellipsoids were not refined. The

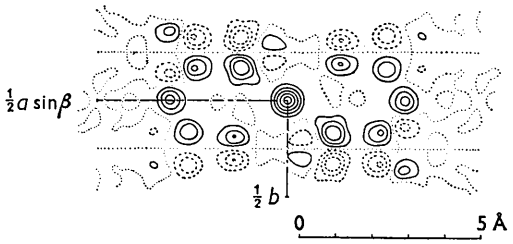


Fig. 2. Cosine part of (hk1) generalized electron-density projection. Contour interval 2 e.Å^{-2} except around the cobalt atom, with the zero contour dotted and negative contours broken. Around cobalt, contour interval 10 e.Å^{-2}.

Table 1. *Anisotropic temperature factors*

The table contains direction cosines of the axes of the vibration ellipsoids referred to the orthogonal crystal axes a, b and c'

	a	b	c'	B (Å^2)	$\sigma(B)$ (Å^2)
Co	+0·9851	−0·0429	+0·1647	2·6	0·05
	−0·0958	+0·7600	+0·6428	2·2	—
	−0·1373	−0·6688	+0·7305	2·8	—
O_1	+0·4040	−0·7150	−0·5700	2·7	—
	+0·1373	+0·6688	−0·7305	3·1	—
	+0·9060	+0·2250	+0·3580	3·2	—
O_2	+0·2570	+0·7059	+0·6600	2·6	—
	+0·1373	+0·6688	−0·7305	3·2	—
	−0·9580	+0·2756	+0·0785	3·3	0·3
O_3	−0·0958	+0·7600	+0·6428	2·8	—
	−0·1373	−0·6688	+0·7305	2·8	—
	+0·9851	−0·0429	+0·1647	5·4	0·4
C_1	+0·4938	+0·6011	+0·6283	2·5	—
	+0·1373	+0·6685	−0·7307	3·0	—
	−0·8680	+0·4410	+0·2282	3·8	0·5
C_2		as for C_1		2·2	—
				2·7	—
				3·5	—
C_3	+0·9851	−0·0429	+0·1647	2·7	0·3
	+0·1373	+0·6688	−0·7305	3·2	—
	−0·0958	+0·7600	+0·6428	3·2	—
C_4	+0·6350	−0·6315	−0·4446	1·9	—
	+0·1373	+0·6688	−0·7305	3·2	—
	+0·7650	+0·4059	+0·5000	3·7	—
C_5		as for C_4		2·2	—
				3·5	—
				4·0	—

Table 2

(a) Final co-ordinates of atoms expressed as fractions of unit-cell edges.
(b) Standard deviations of co-ordinates expressed in Å.
(c) Fractional co-ordinates of hydrogen atoms used for structure factor calculations.

(a)

	x	y	z
Co	0	0	0
O_1	+0·145	+0·219	+0·099
O_2	+0·117	−0·175	−0·088
O_3	+0·050	−0·297	+0·142
C_1	+0·356	+0·340	+0·199
C_2	+0·263	+0·174	+0·113
C_3	+0·309	−0·021	+0·050
C_4	+0·238	−0·176	−0·045
C_5	+0·305	−0·362	−0·100

(b)

	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)
Co	0	0	0
O_1	0·007	0·008	0·011
O_2	0·007	0·009	0·011
O_3	0·008	0·010	0·011
C_1	0·010	0·013	0·016
C_2	0·009	0·013	0·015
C_3	0·009	0·013	0·016
C_4	0·010	0·012	0·015
C_5	0·010	0·013	0·016

(c)

	x	y	z
H_1	+0·31	+0·47	+0·25
H_2	+0·41	+0·45	+0·14
H_3	+0·43	+0·23	+0·27
H_4	+0·41	−0·03	+0·07
H_5	+0·23	−0·47	−0·16
H_6	+0·37	−0·27	−0·15
H_7	+0·36	−0·48	−0·03
H_8	+0·13	−0·41	+0·18
H_9	+0·00	−0·41	+0·19

---

* The positions of the hydrogen bonds (see Fig. 3) suggest co-ordinates for the H atoms of the water molecule different from those assumed for the structure factor calculations and quoted in Table 2(c). However, it was not considered worth while to recalculate structure factors with the positions of two hydrogen atoms changed.

Table 3. *Observed and calculated structure factors*

h	k	ℓ	|F_o|	F_c
0	0	0	-	306
1	0	0	94	84
2	0	0	7	-7
3	0	0	77	71
4	0	0	17	19
5	0	0	<7	1
6	0	0	29	29
7	0	0	38	37
8	0	0	30	30
9	0	0	18	19
10	0	0	8	8
11	0	0	7	5
12	0	0	8	7
13	0	0	9	9
14	0	0	7	6
15	0	0	6	4
16	0	0	8	6
-16	0	2	9	9
-15	0	2	5	7
-14	0	2	<5	3
-13	0	2	10	11
-12	0	2	8	9
-11	0	2	<4	-3
-10	0	2	12	12
-9	0	2	31	33
-8	0	2	39	40
-7	0	2	51	51
-6	0	2	36	37
-5	0	2	23	21
-4	0	2	53	53
-3	0	2	43	44
-2	0	2	18	16
-1	0	2	81	82
0	0	2	78	83
1	0	2	36	34
2	0	2	5	6
3	0	2	10	14
4	0	2	30	31
5	0	2	12	11
6	0	2	11	12
7	0	2	22	22
8	0	2	8	8
9	0	2	11	10
10	0	2	23	22
11	0	2	11	12
12	0	2	10	9
13	0	2	11	11
14	0	2	<5	5
15	0	2	<5	2
-16	0	4	7	8
-15	0	4	<5	5
-14	0	4	9	8
-13	0	4	10	11
-12	0	4	8	10
-11	0	4	15	16
-10	0	4	16	16
-9	0	4	20	19
-8	0	4	32	31
-7	0	4	19	21
-6	0	4	19	19
-5	0	4	46	44
-4	0	4	33	30
-3	0	4	28	30
-2	0	4	35	32
-1	0	4	19	-17
0	0	4	22	-21
1	0	4	17	18
2	0	4	36	38
3	0	4	48	48
4	0	4	40	42
5	0	4	40	39
6	0	4	29	31
7	0	4	<3	1
8	0	4	<4	4
9	0	4	20	22
10	0	4	13	15
11	0	4	10	11
12	0	4	11	12
13	0	4	<5	7
14	0	4	<5	4
-16	0	6	<5	1
-15	0	6	<5	6
-14	0	6	9	10
-13	0	6	4	5
-12	0	6	13	14
-11	0	6	23	25
-10	0	6	13	11
-9	0	6	<4	-1
-8	0	6	<3	5
-7	0	6	14	11
-6	0	6	14	12
-5	0	6	22	22
-4	0	6	54	55
-3	0	6	53	49
-2	0	6	24	23
-1	0	6	17	18
0	0	6	<3	2
1	0	6	31	28
2	0	6	67	64
3	0	6	34	34
4	0	6	25	24
5	0	6	44	48
6	0	6	18	19
7	0	6	<4	-4
8	0	6	11	13
9	0	6	13	14
10	0	6	4	6
11	0	6	5	5
12	0	6	5	6
13	0	6	7	5
-16	0	8	<5	1
-15	0	8	<5	4
-14	0	8	5	6
-13	0	8	5	4
-12	0	8	10	9
-11	0	8	22	22
-10	0	8	13	14
-9	0	8	5	-8
-8	0	8	12	13
-7	0	8	27	31
-6	0	8	9	9
-5	0	8	21	25
-4	0	8	51	48
-3	0	8	35	33
-2	0	8	33	31
-1	0	8	32	29
0	0	8	20	21
1	0	8	33	29
2	0	8	23	21
3	0	8	7	7
4	0	8	9	10
5	0	8	12	12
6	0	8	13	12
7	0	8	7	10
8	0	8	10	9
9	0	8	10	9
10	0	8	<5	3
11	0	8	<5	1
12	0	8	<5	5
-15	0	10	<5	5
-14	0	10	<5	6
-13	0	10	<5	4
-12	0	10	8	8
-11	0	10	13	14
-10	0	10	9	9
-9	0	10	12	13
-8	0	10	23	22
-7	0	10	21	21
-6	0	10	18	20
-5	0	10	13	12
-4	0	10	8	7
-3	0	10	15	14
-2	0	10	17	17
-1	0	10	20	20
0	0	10	24	23
1	0	10	9	10
2	0	10	5	6
3	0	10	4	7
4	0	10	<4	-1
5	0	10	6	5
6	0	10	13	13
7	0	10	13	12
8	0	10	12	10
9	0	10	<5	5
10	0	10	<5	3
-14	0	12	<5	4
-13	0	12	<5	4
-12	0	12	5	6
-11	0	12	<5	2
-10	0	12	6	9
-9	0	12	17	18
-8	0	12	11	10
-7	0	12	7	9
-6	0	12	14	13
-5	0	12	6	4
-4	0	12	4	-4
-3	0	12	<4	2
-2	0	12	20	17
-1	0	12	17	17
0	0	12	6	7
1	0	12	13	12
2	0	12	14	13
3	0	12	6	5
4	0	12	5	7
5	0	12	7	7
6	0	12	8	7
7	0	12	11	10
8	0	12	5	4
-13	0	14	<5	2
-12	0	14	<5	2
-11	0	14	<5	3
-10	0	14	5	6
-9	0	14	7	8
-8	0	14	5	6
-7	0	14	<5	2
-6	0	14	13	11
-5	0	14	13	13
-4	0	14	<5	1
-3	0	14	8	8
-2	0	14	18	18
-1	0	14	5	5
0	0	14	5	4
1	0	14	12	12
2	0	14	10	9
3	0	14	9	7
4	0	14	7	7
5	0	14	<5	4
-10	0	16	<5	4
-9	0	16	<5	5
-8	0	16	<5	3
-7	0	16	<5	4
-6	0	16	10	10
-5	0	16	9	9
-4	0	16	9	8
-3	0	16	7	8
-2	0	16	5	4
-1	0	16	<5	3
0	0	16	<5	3
1	0	16	<5	4
1	1	0	7	9
2	1	0	22	23
3	1	0	13	12
4	1	0	29	29
5	1	0	28	25
6	1	0	5	4
7	1	0	<2	1
8	1	0	6	-7
9	1	0	10	-9
10	1	0	7	9
11	1	0	6	8
12	1	0	<3	-3
13	1	0	<4	1
14	1	0	<4	1
15	1	0	4	-4
16	1	0	<4	-3
0	2	0	17	-16
1	2	0	<2	1
2	2	0	29	33
3	2	0	52	52
4	2	0	40	42
5	2	0	26	28
6	2	0	28	29
7	2	0	19	20
8	2	0	7	5
9	2	0	16	17
10	2	0	21	23
11	2	0	12	12
12	2	0	9	9
13	2	0	7	9
14	2	0	4	5
15	2	0	<4	4
16	2	0	4	4
1	3	0	10	11
2	3	0	<2	1
3	3	0	5	-6
4	3	0	7	-5
5	3	0	11	-11
6	3	0	12	-12
7	3	0	<3	1
8	3	0	4	5
9	3	0	<3	0
10	3	0	<3	1
11	3	0	<3	0
12	3	0	<4	-2
13	3	0	<4	0
14	3	0	<4	2
15	3	0	<4	0
16	3	0	<4	1
0	4	0	21	22
1	4	0	25	28
2	4	0	26	26
3	4	0	16	15
4	4	0	14	16
5	4	0	16	19
6	4	0	17	19
7	4	0	14	16
8	4	0	6	9
9	4	0	7	8
10	4	0	8	8
11	4	0	4	4
12	4	0	7	6
13	4	0	7	7
14	4	0	6	4
15	4	0	<4	3
1	5	0	<3	-3
2	5	0	7	-9
3	5	0	<3	-2
4	5	0	3	3
5	5	0	<3	2
6	5	0	6	5
7	5	0	<3	2
8	5	0	<3	0
9	5	0	<4	1
10	5	0	5	-3
11	5	0	<4	-1
12	5	0	<4	3
13	5	0	<4	0
14	5	0	<4	-1
0	6	0	21	24
1	6	0	7	10
2	6	0	<3	4
3	6	0	13	14
4	6	0	9	10
5	6	0	5	5
6	6	0	6	5
7	6	0	6	6
8	6	0	9	9
9	6	0	7	7
10	6	0	4	4
11	6	0	4	4
12	6	0	4	3
1	7	0	<4	2
2	7	0	<4	4
3	7	0	<4	2
4	7	0	<4	1
5	7	0	<4	0
6	7	0	<4	-1
7	7	0	<4	0
8	7	0	<4	-1
9	7	0	<4	0
10	7	0	<4	3
0	8	0	<4	2
1	8	0	4	3
2	8	0	6	5
3	8	0	6	5
4	8	0	4	4
5	8	0	<4	3
6	8	0	6	6
7	8	0	4	4
-16	1	1	7	6
-15	1	1	5	5
-14	1	1	7	6
-13	1	1	10	10
-12	1	1	8	8
-11	1	1	11	11
-10	1	1	16	15
-9	1	1	18	17
-8	1	1	34	30
-7	1	1	37	34
-6	1	1	18	16
-5	1	1	29	25
-4	1	1	35	36
-3	1	1	13	13
-2	1	1	17	18
-1	1	1	48	54
0	1	1	65	72
1	1	1	44	48
2	1	1	34	31
3	1	1	52	49
4	1	1	35	35
5	1	1	19	17
6	1	1	34	30
7	1	1	27	26
8	1	1	18	18
9	1	1	22	22
10	1	1	15	15
11	1	1	7	8
12	1	1	11	11
13	1	1	8	8
14	1	1	<5	3
15	1	1	5	5
-16	2	1	<5	1
-15	2	1	<5	-1
-14	2	1	<5	1
-13	2	1	<5	0
-12	2	1	<4	-1
-11	2	1	<4	0
-10	2	1	<4	-3
-9	2	1	<4	-1
-8	2	1	4	5
-7	2	1	6	4
-6	2	1	11	9
-5	2	1	7	7
-4	2	1	4	3
-3	2	1	14	12
-2	2	1	16	-14
-1	2	1	29	-30
0	2	1	9	-13
1	2	1	29	-30
2	2	1	3	-2
3	2	1	24	23
4	2	1	13	-13
5	2	1	<3	-1
6	2	1	12	11
7	2	1	14	-14
8	2	1	14	-14
9	2	1	4	4
10	2	1	6	6
11	2	1	<4	3
12	2	1	<5	1
13	2	1	<5	2
14	2	1	<5	2
15	2	1	<5	-2
-16	3	1	<6	2
-15	3	1	<5	2
-14	3	1	5	6
-13	3	1	8	8
-12	3	1	8	7
-11	3	1	10	9
-10	3	1	19	18
-9	3	1	14	12
-8	3	1	7	-8
-7	3	1	15	14
-6	3	1	43	41
-5	3	1	21	20
-4	3	1	34	35
-3	3	1	70	68
-2	3	1	40	41
-1	3	1	20	22
0	3	1	19	19
1	3	1	12	12
2	3	1	37	34
3	3	1	36	36
4	3	1	19	19
5	3	1	23	22
6	3	1	23	22
7	3	1	13	13
8	3	1	5	5
9	3	1	8	7
10	3	1	14	13
11	3	1	6	7
12	3	1	5	4
13	3	1	9	9
14	3	1	5	5
15	3	1	<5	3
-15	4	1	<6	0
-14	4	1	<5	-1
-13	4	1	<5	0
-12	4	1	<5	1
-11	4	1	<5	-1
-10	4	1	<4	1
-9	4	1	<4	0
-8	4	1	6	-6
-7	4	1	<4	-4
-6	4	1	4	-4
-5	4	1	<4	-6
-4	4	1	<3	-3
-3	4	1	6	-5
-2	4	1	<3	3
-1	4	1	11	11
0	4	1	13	16
1	4	1	16	15
2	4	1	<3	-2
3	4	1	6	-5
4	4	1	7	9
5	4	1	<4	-2
6	4	1	7	-6
7	4	1	11	12
8	4	1	8	9
9	4	1	<4	-2
10	4	1	5	-4
11	4	1	<5	-3
12	4	1	<5	-1
13	4	1	<5	0
14	4	1	<5	-1
15	4	1	<6	1
-14	5	1	<6	3
-13	5	1	7	6
-12	5	1	5	4
-11	5	1	<5	2
-10	5	1	8	7
-9	5	1	10	10
-8	5	1	15	14
-7	5	1	16	15
-6	5	1	7	7
-5	5	1	6	5
-4	5	1	9	8
-3	5	1	7	5
-2	5	1	5	3
-1	5	1	17	16
0	5	1	28	27
1	5	1	15	16
2	5	1	5	6
3	5	1	15	14
4	5	1	15	16
5	5	1	10	9
6	5	1	15	14
7	5	1	15	15
8	5	1	9	10
9	5	1	8	9
10	5	1	5	7
11	5	1	5	5
12	5	1	<5	5
13	5	1	<5	4
14	5	1	<6	3
-13	6	1	<6	0
-12	6	1	<5	1
-11	6	1	<5	-1
-10	6	1	<5	0
-9	6	1	5	4
-8	6	1	<5	1
-7	6	1	<5	-1
-6	6	1	<5	2
-5	6	1	<4	1
-4	6	1	<4	-1
-3	6	1	<4	3
-2	6	1	4	4
-1	6	1	4	-5
0	6	1	6	-7
1	6	1	4	-2
2	6	1	6	-4
3	6	1	4	-4
4	6	1	<4	3
5	6	1	<5	1
6	6	1	<5	-2
7	6	1	<5	0
8	6	1	<5	-1
9	6	1	<5	-2
10	6	1	<5	3
11	6	1	<5	3
12	6	1	<6	0
-11	7	1	6	4
-10	7	1	<6	4
-9	7	1	<5	2
-8	7	1	6	5
-7	7	1	5	5
-6	7	1	5	4
-5	7	1	10	9
-4	7	1	12	11
-3	7	1	9	8
-2	7	1	7	8
-1	7	1	8	7
0	7	1	8	7
1	7	1	8	8
2	7	1	8	8
3	7	1	8	9
4	7	1	8	6
5	7	1	<5	3
6	7	1	<5	3
7	7	1	<5	3
8	7	1	<5	3
9	7	1	8	5
10	7	1	<6	4

computation and refinement were made on the Pegasus electronic digital computer using programmes devised by Dr H. J. Milledge. These programmes can handle only 7 different anisotropic temperature factors, and it is because of this restriction that identical ellipsoid orientations have been assigned to the pairs of atoms C_1 and C_2, C_5 and C_4. The programme also requires the anisotropic B values to be the same for C_1 and C_2. However, it was possible to give C_1 a temperature factor larger than that of C_2 by applying an additional isotropic factor to its atomic scattering factor. Thus the B values for C_1 all exceed those for C_2 by the same amount, viz. 0·3 Å^2. This is a reasonable approximation because one would expect the vibration ellipsoids of bonded atoms to be related. The same applies to C_5 and C_4. The refinement of the two ellipsoids was carried out using C_1 and C_5, it being assumed that C_2 and C_4 would follow them closely. For carbon and oxygen, the McWeeny (1951) atomic scattering factor curves were used, and for cobalt the scattering factors prepared by Dr J. A. Ibers for Volume 3 (not yet published) of *International Tables for X-ray Crystallography.*

Of the three sets of intensities measured, the $h0l$ reflexions were used to refine x- and z-co-ordinates and $hk1$ to refine x- and y-co-ordinates. The $hk0$ intensities were not considered suitable for diagonal least-squares refinement because of the overlap of atoms in the (001) projection. Using an $hk1$ generalized projection the overlap is removed and so one would expect the refinement of $hk1$ data to converge more quickly than that of $hk0$. The final co-ordinates are given in Table 2(a) and the temperature factors in Table 1. Structure factors calculated from these values are listed in Table 3. The conventional residual error factors R for the three sets of intensities are: $h0l$ 0·069, $hk0$ 0·090, $hk1$ 0·074. In calculating these R factors, all reflexions were used, including those which may be affected by extinction and those too weak to be observed. The unobserved reflexions were dealt with in the following way. If $|F_c| > |F'_o|$ where $|F'_o|$ is the minimum that it would be possible to observe, then $|F_c|-|F'_o|$ was added to $\Sigma||F_c|-|F_o||$; if $|F_c| \le |F'_o|$, nothing was added. In either case, $\frac{1}{2}|F'_o|$ was added to $\Sigma|F_o|$. Throughout the refinement, better agreement was obtained for $hk1$ reflexions than for $hk0$. This may be partly due to the greater weight given to refinement of $hk1$ data but probably also indicates that the $hk0$ intensities are less accurate than $hk1$. This is expected because, when using Mo K radiation, strong white radiation streaks appear on the photographs. On a zero-layer photograph, the streak from a strong reflexion passes through and obscures other orders (both higher and lower) of the same reflexion. On an upper-layer photograph, the streaks usually pass *between* other reflexions so that for accurate work it is an advantage to use upper-layer instead of zero-layer intensities. Standard deviations of co-ordinates, calculated from the formula given in equation (1) of Ibers & Cromer (1958), using unit weights, are given in Table 2(b). The order $\sigma(x) < \sigma(y) < \sigma(z)$ obtained for each atom reflects the fact that all 3 sets of data were used to calculate $\sigma(x)$, only 2 sets, $hk0$ and $hk1$ for $\sigma(y)$, and only $h0l$ for $\sigma(z)$. A root-mean-square of $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ was taken as the standard deviation $\sigma(r)$ of each atomic position. Bond lengths and angles are shown in Table 4 together with their standard deviations calculated using formulae given by Jeffrey & Cruickshank (1953). There is also an additional uncertainty of about 0·3% in the absolute values of the bond lengths owing to the experimental error in measuring the unit-cell constants. This will not affect their relative values.

Table 4. *Bond lengths and bond angles with standard deviations given in brackets*

Values marked * have been corrected for error due to thermal vibration

Atoms primed (′) lie in molecule with its centre at (0, −1, 0) and atoms doubly primed (″) lie in molecule with its centre at (0, $-\frac{1}{2}$, $\frac{1}{2}$)

Co–O_1	2·05* (0·01) Å	O_1–Co–O_2	92·0° (0·4)
Co–O_2	2·06* (0·01)	O_1–Co–O_3	91·6 (0·4)
Co–O_3	2·23* (0·01)	O_2–Co–O_3	87·1 (0·4)
C_2–O_1	1·28 (0·02)	Co–O_1–C_2	124·2 (0·8)
C_4–O_2	1·27 (0·02)	Co–O_2–C_4	122·6 (0·8)
C_1–C_2	1·49 (0·02)	O_1–C_2–C_1	116·7 (1·1)
C_5–C_4	1·47 (0·02)	O_1–C_2–C_3	123·9 (1·1)
C_2–C_3	1·43 (0·02)	C_1–C_2–C_3	119·4 (1·1)
C_4–C_3	1·41 (0·02)		
		O_2–C_4–C_5	115·3 (1·1)
		O_2–C_4–C_3	125·5 (1·2)
		C_5–C_4–C_3	119·2 (1·1)
		C_2–C_3–C_4	127·9 (1·2)

Angles involving hydrogen bonds:

Co–O_3–O'_1	124·1°	Co′–O'_1–O_3	110·6°
Co–O_3–O''_2	136·4	C'_2–O'_1–O_3	123·1
O'_1–O_3–O''_2	97·3		
		Co″–O''_2–O_3	120·8
		C''_4–O''_2–O_3	109·2

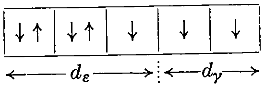
For some temperature factors, standard deviations calculated from

$$\sigma^2(B_i) = \sum_j (\Delta F_j)^2/[(n-s)(\sum_j (\partial F_j/\partial B_i)^2)]\,,$$

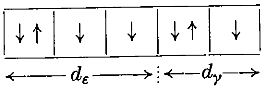
where n is the number of observations and s the number of variables, have been quoted in Table 1. This formula cannot be used if the direction of B lies far from the plane of the set of reflexions. Since some ellipsoid axes are almost equally inclined to a, b and c^*, the standard deviations could not be estimated, (this means, too, that the refinement of these thermal factors was not reliable, and it was necessary to use a greater measure of personal judgment in estimating their shifts).

Discussion

The co-ordination polyhedron of oxygen atoms around cobalt in this structure is a tetragonally distorted octahedron, the Co–O bond lengths in the ring being 2·05–2·06 Å and the Co–H_2O bond lengths 2·23 Å. The difference of 0·17 Å between these bonds is highly significant in view of the bond length s.d. 0·01 Å. In so far as there is covalent binding, $4s4p^34d^2$ orbitals of the cobalt atom would be used. The hybridization would be such that $4s4p^24d$ hybrid orbitals would make the greater contribution to the bonds with the acetylacetone chelate groups in the square plane and $4p4d$ hybrids to the longer bonds with the water molecules. The formation of a weaker, longer bond with a water molecule may be interpreted in terms of the lower electronegativity of its oxygen atom as compared with that of the acetylacetone oxygen, or in terms of ligand-field theory. The latter has been used to account for the large distortions from regular octahedral co-ordination in compounds such as MnF_3 (Hepworth & Jack, 1957) and $CuCl_2.2\,H_2O$ (Dunitz & Orgel, 1957). In these compounds, two of the metal–ligand bonds are considerably longer than the other four, and this lengthening is attributed to asymmetry of the $3d_\gamma$ sub-shell of the metal which contains 1 electron in MnF_3 and 3 electrons in $CuCl_2.2\,H_2O$. A deviation from perfect octahedral co-ordination may also arise from asymmetry of the $3d_\varepsilon$ sub-shell (Gillespie & Nyholm, 1957) though the effect is expected to be small because the d_ε orbitals point between the directions of the octahedral bonds. High-spin Co(II) has the $3d$ shell configuration



in which the d_γ sub-shell is symmetrically filled but the d_ε sub-shell is asymmetric. The distortion observed in cobalt(II) bisacetylacetone dihydrate (magnetic moment $4{\cdot}9\mu_B$) might be attributed to the d_ε asymmetry, but it seems that it is larger than that expected to arise from this effect alone. A more likely explanation is that there is asymmetry of the d_γ sub-shell owing to some mixing-in of the configuration



which is consistent with the large spin-orbit coupling in this and other cobalt(II) complexes.

It would be interesting to test these deductions by comparing the bond-lengths in similar compounds of cobalt and other transition metals, but there are few reports of sufficiently accurate structure determinations. For cobalt acetate tetrahydrate, van Niekerk & Schoening (1953) find two Co–O bonds of length 2·12 Å and four Co–H_2O bonds, two of which are 2·06 Å long and the other two 2·11 Å long, but these values are obtained from a study of nickel acetate tetrahydrate with which the cobalt compound is isomorphous. The similarity of these bond lengths may not be significant. In cobalt chloride dihydrate (Weinstein, 1949) the two Co–H_2O bonds are short (1·93 Å) and it is the four Co–Cl bonds (2·53 Å) which are longer than one would expect.

In compounds of Ni(II) (d^8) and Zn(II) (d^{10}), both d_ε and d_γ are symmetric so that here one might expect regular octahedral co-ordination. For the latter metal, mixing-in of a configuration involving asymmetry of d_γ is impossible, but for Ni(II) it could take place. Again, the few results available either are not sufficiently accurate or are contradictory. For nickel acetate tetrahydrate, it is doubtful whether the bond lengths are accurate enough to show distortion (see above). There is no appreciable distortion in zinc acetate dihydrate (Zn–O 2·17–2·18 Å and Zn–H_2O 2·14 Å) (van Niekerk, Schoening & Talbot, 1953) but this is in contrast to the long Zn–H_2O bonds (2·27 Å) in zinc 8-hydroxyquinoline dihydrate (cf. Zn–O 2·05 Å and Zn–N 2·06 Å in the same compound) (Merritt, Cady & Mundy, 1954).

The other bond lengths in the molecule agree well with generally accepted values, the differences in length between chemically identical bonds being within experimental error. The lengths of C_1–C_2 and C_4–C_5 are less than 1·54 Å as one would expect for bonds between a methyl carbon and a trigonally hybridized carbon. The similarity of the lengths of the bonds formed by O_1 and O_2 supports the view that there is no difference chemically between these atoms once chelation has taken place. The five atoms O_1, C_2, C_3, C_4, and O_2 of the acetylacetone ring are very nearly coplanar. The equation of their mean plane is given in Table 5 together with the distances from the plane of all atoms except O_3. The deviations from planarity are small except for C_1 and Co. It is interesting that the whole ring is not planar, the Co atom lying 0·4 Å away from the plane of the 5 lighter atoms. (Note that the orientations of the vibration ellipsoids were chosen with reference to the mean plane of all 6 atoms forming the ring, which is not the plane quoted in Table 5.)

The molecules are linked together by two series of hydrogen bonds. One series, length 2·90 Å, runs approximately parallel to *b*, linking O_3 and O_1 in molecules separated by the lattice translation *b*, and the other series, length 2·91 Å, runs approximately parallel to c^*, linking O_3 and O_2 in molecules related

Table 5. *Equation of mean plane of acetylacetone ring referred to orthogonal crystal axes a, b and c′*

All expressed in Å units, together with distances of atoms from the mean plane

$$-0{\cdot}265x-0{\cdot}672y+0{\cdot}691z'+0{\cdot}424 = 0$$

O_1	+0·03 Å	C_1	−0·20 Å
O_2	−0·01	C_5	+0·03
C_2	−0·04	Co	+0·42
C_3	+0·02		
C_4	+0·00		

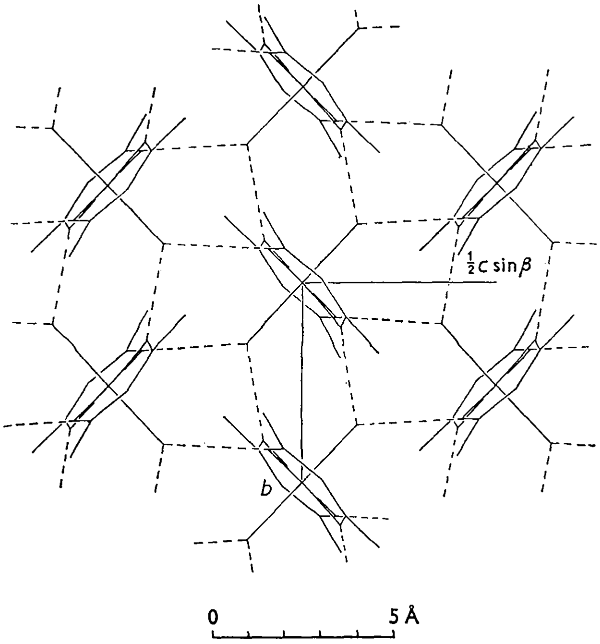


Fig. 3. A layer of molecules parallel to (100) showing hydrogen bonds (broken lines). All cobalt atoms in the layer have $x = 0$.

by the glide plane. The hydrogen bonds bind the molecules into layers parallel to (100); one of the layers is shown in Fig. 3. The angles at each oxygen atom between hydrogen bonds and other bonds are listed in Table 4. Joining the layers are van der Waals forces between $-CH_3$ and $-CH$ groups. This arrangement explains the cleavage parallel to (100) and the difficulty in cutting crystals along (010) without producing distortion. Distances of closest approach between non-bonded atoms are

(i) within a hydrogen-bonded layer: $O \cdots H_2O$ 3·34 Å, $H_2O \cdots CH_3$ 3·52 Å, $O \cdots CH_3$ 3·86 Å, $C \cdots CH_3$ 3·53 Å, $CH \cdots CH_3$ 3·80 Å, $CH_3 \cdots CH_3$ 3·56 Å, and

(ii) between layers: $CH \cdots CH_3$ 4·02 Å, $CH_3 \cdots CH_3$ 4·06 Å.

The molecules are thus drawn closer to each other within a layer than they are between layers. This is probably due to the presence of the hydrogen bonds, though one cannot draw definite conclusions without knowledge of the positions of the hydrogen atoms of the $-CH$ and $-CH_3$ groups.

The values of the anisotropic temperature factors indicate a libration of the molecule about the normal to the mean plane of the Co–acetylacetone rings. For each atom except cobalt, the direction of the smallest B lies either along a bond or bisects the obtuse angle between two bonds; the normal to the plane is the direction of the medium B factor. The thermal anisotropies of the carbon atoms are on the whole larger than those of O_1 and O_2. For the cobalt atom, the largest B lies along the bond to the water molecule; this bond is longer and therefore weaker than the other Co–O bonds. The atom with the greatest thermal anisotropy is O_3, the water molecule. The distortion is so large that it can easily be seen in the electron-density projection on (010), Fig. 1, the peak being very elongated. The direction of the largest B factor, nearly along the a axis, is perpendicular to the O_3–Co bond and also nearly perpendicular to the hydrogen bonds joining O_3 to O_1 and to O_2. Thus the water molecule is restrained in the directions of the O_3–Co and hydrogen bonds but it can vibrate considerably in the direction perpendicular to the bonds. The large thermal vibration of O_3 will cause an error in its position and hence in the length of the Co–O_3 bond (Cruickshank, 1956). The bond-length error y is given by

$$y = \frac{1}{2r}\left(\frac{s^2}{1+s^2/q^2} + \frac{t^2}{1+t^2/q^2}\right)$$

where r is the distance of O_3 from the centre of the molecule, s^2 and t^2 are the mean square amplitudes of vibration in the direction of the two ellipsoid axes which are perpendicular to the bond, and q^2 is the Gaussian breadth parameter for the peak. For $B_3 =$ 5·4 Å^2, $s^2 = 0{\cdot}068$ Å^2, and for $B_1 = 2{\cdot}8$ Å^2, $t^2 =$ 0·035 Å^2. Taking as a reasonable value $q^2 = 0{\cdot}2$ Å^2, we find $y = 0{\cdot}018$ Å. The Co–O_3 bond length is then increased to 2·23 Å. Corrections calculated in the same way for O_1 and O_2 are 0·015 Å, so that the correction does not alter significantly the differences between bond lengths. For the carbon atoms, which are farther from the molecular centre, the corrections will be considerably smaller and the other bond lengths will not be changed.

I wish to thank Prof. Dame Kathleen Lonsdale, F.R.S. and Prof. R. S. Nyholm, F.R.S. for their valuable advice; Dr Naida Gill for supplying the compound; Messrs. Babcock & Wilcox Ltd. for the gift of the use of their Pegasus computer on which much of the calculation was performed; and the University of London for the award of a Turner & Newall Research Fellowship.

References

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 757.
Dunitz, J. D. & Orgel, L. E. (1957). *Nature, Lond.* **179**, 462.
Gillespie, R. J. & Nyholm, R. S. (1957). *Quart. Rev. Chem. Soc. Lond.* **11**, 339.
Hepworth, M. A. & Jack, K. H. (1957). *Acta Cryst.* **10**, 345.
Iball, J. (1954). *J. Sci. Instrum.* **31**, 71.
Ibers, J. A. & Cromer, D. T. (1958). *Acta Cryst.* **11**, 794.
Jeffrey, G. A. & Cruickshank, D. W. J. (1953). *Quart. Rev. Chem. Soc. Lond.* **7**, 335.
McWeeny, R. (1951). *Acta Cryst.* **4**, 513.
Merritt, L. L., Cady, R. T. & Mundy, B. W. (1954). *Acta Cryst.* **7**, 473.
Niekerk, J. N. van & Schoening, F. R. L. (1953). *Acta Cryst.* **6**, 609.
Niekerk, J. N. van, Schoening, F. R. L. & Talbot, J. H. (1953). *Acta Cryst.* **6**, 720.
Weinstein, B. K. (1949). *Doklady Akad. Nauk*, **68**, 301.