Inorganica Chimica Acta, 25 (1977) 33–39
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

The Crystal Structure of Dimeric Bis(acetylacetonato)iron(II)

S. SHIBATA, S. ONUMA, A. IWASE and H. INOUE
Department of Chemistry, Shizuoka University, Oya, Shizuoka 422, Japan
Received January 22, 1977

The crystal structure of anhydrous bis(acetylacetonato)iron(II) has been determined by X-ray diffraction. The crystal is monoclinic with space group $P2_1/c$, a = *14.95(2),* b = *8.51(1),* c = *19.03(2)* Å, *and* β = *105.1(1)°, with four dimeric molecules in the unit cell. The final R value is 0.109 for data from 1365 counter-collected reflections. In the dimeric molecules an octahedrally coordinated Fe atom is linked through three shared oxygen atoms to the second iron atom located within a square pyramid. The Fe–Fe distance is 3.028* Å. *There are two different groups of Fe–O distances, with average values of 2.04 and 2.25* Å. *The bond lengths and angles of the chelating ligands are almost the same as previously reported values.*

Introduction

Several X-ray diffraction studies have shown that bisacetylacetonato complexes of divalent first-transition metals are polymeric in the crystalline state, this being in contrast with their monomeric nature in the gaseous state [1]. Nickel and cobalt acetylacetonates are trimeric [2] and tetrameric [3], respectively, but with both oligomers containing octahedrally coordinated metal atoms. Zinc acetylacetonate is also trimeric [4]. The characteristic feature of this oligomer is that the central metal is coordinated octahedrally, but the other terminal metal atoms are coordinated pentagonally. However, the structure of bis(acetylacetonato)iron(II) has remained uncertain in spite of considerable interest. Buckingham and coworkers [5] suggested that on evidence from molecular weight measurements the compound would be hexameric in the solid state and that from a comparison of its X-ray powder pattern with those for the nickel and cobalt acetylacetonates its structure would be centrosymmetric. Therefore, a single crystal X-ray structure analysis was undertaken in order to clarify the molecular structure of anhydrous ferrous acetylacetonate in the crystalline state.

Experimental

Bis(acetylacetonato)iron(II) was prepared by the reaction of ferrous sulphate with acetylacetone under nitrogen [5]. Special care was taken in handling the sample because the compound is highly susceptible to oxidation in air. Crystals of the black compound were obtained by repeated sublimation at 170 °C and 10^{-4} torr. A suitable crystal of dimensions 0.3 × 0.2 × 0.1 mm was selected and sealed in a thin-walled glass capillary tube. Preliminary photographic data showed that the crystal belonged to the monoclinic system. Unit cell dimensions were determined by a least-squares method using ten reflections measured on a Rigaku automatic four-circle single-crystal diffractometer with MoKα_1 radiation (λ = 0.70926 Å). The density of the crystal was measured by flotation (aq. KI). The crystal data are given in Table I.

The intensity data were collected on the same diffractometer with graphite monochromatized MoKα radiation at room temperature. The ω–2θ scan technique was employed at a speed of 4°/min in 2θ, and within the range of $2\theta < 40°$. Appreciable decomposition of the crystal was noticeable. Therefore, the intensities of three reference reflections (002, $\bar{1}02$, 020) were monitored for every 50 reflection measurements and used for the correction of the measured intensities. The data were also corrected for the Lorentz and polarization factors. Reflections for which the amplitude | F | was less than three times the standard deviation were not used in the subsequent calculations. The number of independent reflections used was 1365.

Structure Determination

The crystal structure was solved by Patterson and Fourier methods. Positional and anisotropic thermal parameters of non-hydrogen atoms were refined by a block-diagonal least-squares procedure. The quantity minimized was $\Sigma\omega\Delta F^2$, where $\Delta F = |F_o| - |F_c|$, and the weighting function ω was 1.0 for $F_o > 20.0$, and 0.2 otherwise. At the final stage the values

TABLE I. Crystal Data.

$[Fe(acac)_2]_2$, $Fe_2C_{20}H_{28}O_8$	
Formula Weight = 508.1	
Monoclinic	
a = 14.95(2) Å	
b = 8.51(1)	
c = 19.03(2)	
β = 105.1(1)°	
Space Group = $P2_1/c$	
Volume of a Unit Cell	= 2338(4) Å^3
Density = 1.48 g cm^{-3}	(flotation)
1.44	(calculated for Z = 4)

of $R = \Sigma \mid \Delta F \mid / \Sigma \mid F_o \mid$ and $R_\omega = [\Sigma\omega(\Delta F)^2 / \Sigma F_o^2]^{1/2}$ were 0.109 and 0.101, respectively. The difference Fourier map was flat and unreasonable electron density regions did not appear, though no evidence of the hydrogen atoms was obtained.

The atomic scattering factors were taken from Ref. 6. Most of the calculations were carried out using UNICS Programs [7] at the Computer Center of the University of Tokyo. The refined parameters of atoms, the numbering of which is indicated in Figure 1, are listed in Table II. Observed and calculated structure factors are listed in Table III.

Results and Discussion

Anhydrous bis(acetylacetonato)iron(II) is neither hexameric nor centrosymmetric as suggested by Buckingham *et al.* [5], but is dimeric in the crystalline state. Figure 1 shows the projection of the dimer along the b axis. The four chelate rings are labeled A, B, C and D. Bond lengths and angles are listed in Table IV and V, respectively; they are grouped according to their chemical equivalence.

The coordination polyhedron for Fe(1) can be described as a distorted octahedron having O(11), O(12), O(22) and O(32) in the equatorial positions and O(21) and O(42) in the axial positions. The axial angle is distorted to 170°, and the *trans* equatorial O–Fe–O angles are 158 and 159°. The average value of the equatorial O–Fe–O angles is 89° (73–108°).

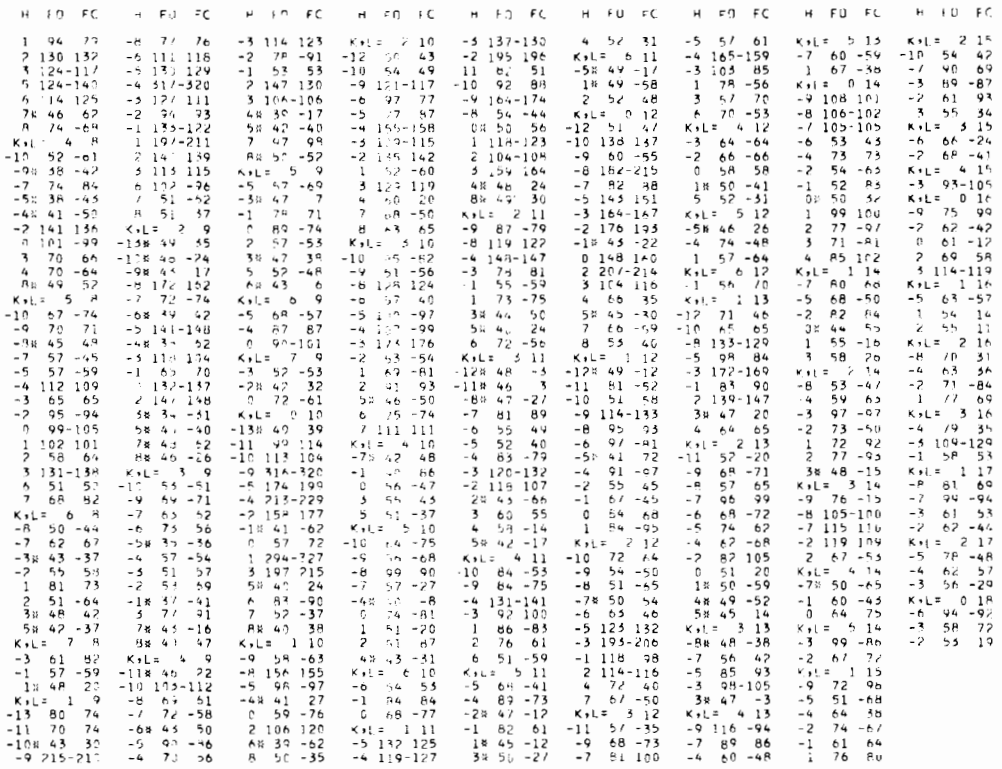
TABLE II. Final Atomic Parameters and Their Estimated Standard Deviations for the Last Digit.[a] (× 10^4)

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	2043(2)	4637(4)	4298(2)	52(2)	134(6)	36(1)	5(7)	39(3)	19(5)
Fe(2)	3903(2)	4271(4)	3960(2)	59(2)	108(5)	37(1)	−38(6)	46(3)	−37(5)
O(11)	2595(10)	5347(20)	3452(8)	49(9)	236(35)	43(6)	−116(31)	10(12)	−87(25)
O(12)	906(10)	3958(17)	3502(10)	74(11)	161(31)	43(6)	−32(29)	69(14)	36(23)
C(11)	2761(17)	6132(30)	2265(13)	97(19)	257(60)	44(10)	−149(56)	126(25)	−25(42)
C(12)	2195(15)	5469(24)	2781(12)	58(15)	71(37)	51(10)	−47(42)	15(20)	−112(34)
C(13)	1265(15)	5066(25)	2435(11)	64(15)	129(42)	34(9)	−37(42)	39(19)	22(32)
C(14)	710(16)	4341(29)	2833(12)	74(16)	170(46)	35(9)	−50(51)	27(20)	1(37)
C(15)	−297(16)	3905(34)	2398(14)	55(18)	323(72)	45(11)	−74(55)	15(23)	−71(46)
O(21)	1387(11)	6536(19)	4583(8)	68(11)	179(31)	49(7)	−25(31)	63(14)	−8(25)
O(22)	1963(9)	3592(17)	5235(7)	59(10)	164(29)	23(5)	13(28)	9(12)	9(21)
C(21)	504(17)	8217(29)	5183(16)	70(18)	152(47)	87(16)	67(50)	95(29)	45(45)
C(22)	1018(14)	6669(28)	5118(12)	38(14)	186(46)	39(9)	−20(43)	28(18)	−9(38)
C(23)	1108(16)	5563(30)	5685(13)	61(16)	160(46)	55(12)	43(49)	26(21)	16(41)
C(24)	1560(16)	4190(32)	5726(14)	64(16)	241(55)	64(12)	−32(51)	118(24)	3(45)
C(25)	1646(22)	2993(34)	6352(13)	158(28)	259(64)	32(10)	−64(68)	89(28)	38(41)
O(31)	4787(9)	6025(16)	3951(8)	47(9)	126(27)	45(6)	−9(25)	42(12)	−12(22)
O(32)	3568(8)	5411(18)	4821(7)	37(8)	207(30)	25(5)	27(27)	29(10)	10(22)
C(31)	5793(16)	8192(28)	4255(12)	68(16)	171(47)	35(10)	−94(47)	40(21)	−24(36)
C(32)	5063(15)	7120(24)	4411(11)	59(15)	87(38)	28(9)	32(39)	−5(18)	11(29)
C(33)	4726(13)	7349(24)	5027(11)	37(14)	97(37)	29(8)	−8(38)	1(17)	3(30)
C(34)	3976(14)	6655(27)	5216(11)	37(13)	131(42)	25(8)	−14(37)	−28(16)	33(29)
C(35)	3589(15)	7133(26)	5832(11)	65(15)	181(47)	30(9)	9(44)	90(19)	−26(34)
O(41)	4117(10)	2787(17)	3208(8)	71(11)	135(28)	42(7)	−8(28)	53(14)	12(23)
O(42)	2974(10)	2630(17)	4142(8)	51(8)	158(27)	29(5)	−30(29)	29(11)	−32(22)
C(41)	4278(20)	497(29)	2529(13)	143(25)	133(46)	50(12)	62(58)	94(28)	−95(40)
C(42)	3894(16)	1321(28)	3074(13)	64(17)	165(48)	45(11)	31(46)	12(22)	54(37)
C(43)	3319(16)	525(29)	3439(13)	75(17)	142(45)	45(10)	31(50)	31(21)	−18(39)
C(44)	2832(16)	1172(25)	3894(13)	58(16)	107(43)	51(12)	30(42)	−36(22)	0(35)
C(45)	2127(17)	243(30)	4194(13)	76(17)	226(52)	36(10)	−117(53)	29(20)	23(39)

[a]Anisotropic thermal factors are of the form: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

TABLE III. Observed and Calculated Structure Factors (×2.5). Asterisks indicate reflections with $\omega = 0.2$, otherwise $\omega = 1.0$.

H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC
K=L= 0 0	-11* 39 40	-4* 29 -15	8* 38 -30	3 169-166	-8 97 112	-3 131 127	11* 40 29	8* 55 46	
2 160-174	-10* 34 36	-3 215-239	10 58 54	4* 28 -6	-7 64 -68	-1 80 -80	K=L= 3 6	7* 40 50	
3 164-181	-9 102-113	-2 152 170	K=L= 6 2	6* 31 -26	-6 89 -98	0 110 -91	-9 92 87	9* 45 -59	
4 247-259	-7* 39 -38	-1 589-622	-7* 45 -78	10* 39 33	-5 55 -49	1 72 64	-8 111-105	10 74 -69	
5 263 268	-6 120 128	0 395 416	-3 87 104	K=L= 6 3	-3 50 51	2 81 73	-7 70 73	K=L= 4 7	
6 128-122	-5 117 121	1 401 445	-2 118-125	-9* 35 21	-1 173-163	3 70 54	-6 177-181	-9 92 94	
7 163-165	-4 224-250	2 311-324	-1 116 115	-8* 42 -38	2 188 186	5 84 -86	-5* 50 -43	-8 57 -80	
8 64 59	-3 59 49	3 227-222	1* 28 -11	-6* 45 -19	3 97 -93	6 133 129	-4 360 366	-7 56 -46	
9 86 -91	-2 236 227	4 142-153	2 116 99	-5 117 126	4 54 -56	8 59 -53	-3 129-135	-5 106-102	
10 208 207	-1 161 161	5 194 199	3 110-111	-3 104-104	5* 38 -57	9* 49 -52	-2 122 121	-4 211 214	
11* 43 -25	1* 37 25	6 303 300	5* 27 18	0 162 160	6 80 72	10* 43 -40	-1 102 -90	-3 81 -81	
12 95-101	2 83 73	7 239-248	6* 47 -57	2 155-141	7* 38 34	11* 50 39	0 100 -97	-1* 42 -57	
K=L= 1 0	3 132 120	9 75 -76	8 55 -71	5 63 61	9 62 -57	K=L= 4 5	1 173 167	0 73 -81	
1 201-219	4* 35 -29	10* 38 35	K=L= 7 2	K=L= 7 3	K=L= 5 4	-11 72 -66	2 82 -78	1 226 217	
2 133 148	5 79 93	11 148 143	-7* 39 -54	-7* 30 -45	-11 71 -61	-9* 43 51	3 52 -53	2* 33 -7	
4 186 162	6 299-289	12 118-105	-6 60 76	-6* 30 -1	-10 99 110	-8* 40 -63	5 122-123	3 130-127	
5* 27 24	7 51 -56	K=L= 1 2	-5 60 67	-5* 48 60	-7 65 -62	-6 180-186	6 171 175	4* 46 59	
6 86 -88	8* 49 -42	-11* 38 31	-4* 35 -46	-4 60 -74	-6 111-116	-5* 40 58	7 95-102	5 102-100	
7* 41 37	9 90 88	-10 106 106	-3 106-108	-3* 31 43	-5 168 182	-4 228 223	8* 31 9	6 126 133	
8 89 -95	10 89 76	-9 94 -89	-1* 34 32	-2 81 -84	-4 75 80	-3 131-131	K=L= 4 6	7* 36 40	
9 189 191	11* 48 -46	-7 54 46	1* 34 -8	-1* 42 30	-3 90 -92	-2 99 92	-11* 40 -34	8 52 -44	
11* 40 -31	13* 36 20	-6 87 -98	2 58 -48	0 69 72	-2* 50 -50	-1 109-103	-10* 43 -49	K=L= 5 7	
12* 29 15	K=L= 3 1	-5 85 97	4 88 84	1 53 -50	-1 55 -64	0 71 55	-9* 35 -8	-7 103 98	
K=L= 2 0	-12* 46 -46	-4 176-195	K=L= 8 2	2 74 66	0 211 194	1 221 218	-8 80 81	-6 66 -92	
0 370 346	-8* 38 -37	-3* 31 -38	-2* 35 -49	3* 31 -33	1 118 109	2 200-189	-7 71 69	-5 61 -67	
1 119 126	-7* 50 -57	-2 59 -60	K=L= 1 3	4* 32 -23	2 246-217	3* 32 -19	-6 60 -61	-2 123 116	
2 278-292	-6 120-133	-1 87 -90	-14 54 56	5 75 61	3 72 -78	4* 38 -20	-5 79 -69	-1 76 -89	
3 72 -62	-5 134 145	0 243 230	-11 130-124	6 61 -66	4* 40 -39	5* 33 -48	-4 88 85	0* 40 -14	
4* 36 -30	-4 84 97	1 96 -81	-9 137 134	K=L= 8 3	5* 29 51	6 172 183	-3 92 88	1* 34 23	
5 202 218	-3 132 149	2 107-111	-8* 33 -28	-2* 42 -19	6 62 68	7 78 -89	-2 114 111	2 63 -57	
6 69 -58	-2 119-147	3 553 548	-6 95-107	K=L= 0 4	7* 42 -32	8* 33 1	-1 215-203	3* 45 57	
7 181-183	-1 113-107	4 101 -98	-4 163 164	-14 73 57	8* 40 -37	K=L= 5 5	0 51 -58	4 84 -93	
9 51 54	0* 24 15	6 172-167	-3 177-155	-11 162-162	K=L= 6 4	-9* 46 -33	2 92 95	6 65 34	
10 52 49	1 128 128	7 68 -61	-2 162 155	-10 99 -99	-9 62 -64	-8 75 86	3* 36 36	K=L= 6 7	
11* 26 18	3* 22 20	8* 35 -34	-1 153-155	-9 167 162	-8 85 93	-6 61 -74	7* 42 61	-9 70 73	
12 70 -67	4* 27 31	10 68 63	0 71 69	-7 92 -87	-7* 32 -32	-5 76 79	9 71 -74	-8* 37 16	
K=L= 3 0	5 93 90	12 55 -55	1 101 100	-6* 35 -52	-6* 32 -22	-4* 31 -39	K=L= 5 6	-6 61 -58	
1 168-186	6* 44 42	K=L= 2 2	2 363-336	-4 244 214	-4 103-101	-1 182-167	-11 52 -70	-5* 43 33	
2* 41 48	7 81 -74	-11* 35 -45	3 151 118	-3 287 258	-3 53 55	0 103 90	-9 63 82	-4* 46 35	
3 135-147	8 55 -48	-10 82 85	4 279-277	-2 87 95	-2 86 -86	1 67 -64	-8* 47 -55	0* 37 -31	
4 146 136	9* 30 23	-9* 39 45	5 59 57	-1 121 133	0 139 127	2 161 154	-6 77 -73	1 108 101	
5 53 63	11 57 57	-8 59 64	6 351 348	1 320 322	1* 32 -37	4 106 -90	-4 177 174	2 53 32	
6 225-230	12* 38 -32	-7* 41 -56	7* 30 -33	2 188 176	2 121 108	5* 46 43	-3* 49 -52	3 76 -76	
7* 46 56	K=L= 4 1	-6 233-239	10* 31 -15	3 315-335	4 85 -89	6* 29 -18	-2* 38 -33	4* 48 -29	
9 92 90	-12 67 -66	-5 193 194	11 105 95	4 87 -97	5* 29 28	K=L= 6 5	-1 54 -48	5 68 41	
10* 43 57	-11 76 77	-4 119 119	12* 42 -42	5 80 -89	6* 44 -41	-4 61 62	1 255 230	6* 36 20	
11 76 -68	-10* 42 41	-3* 21 15	K=L= 2 3	6 137 140	7* 35 25	-3* 46 8	2 78 -63	K=L= 7 7	
12* 49 29	-9 110-117	-2 107-101	-12* 34 -35	7* 39 48	K=L= 7 4	-2 91 -96	3 124-129	-2* 41 38	
K=L= 4 0	-8* 32 39	-1 347-325	-10 121 133	8 69 -70	-7 76 -80	0 64 62	6 92 95	-1* 42 -43	
1* 42 -41	-7 134-151	0 147-119	-9* 25 2	10 58 -64	-6* 33 -47	1 161 167	7* 42 29	0 58 58	
2 123-125	-6 93 106	1 384 324	-7 91 98	11 106 89	-5 86 87	2 99 -94	8 58 -65	2* 45 -45	
3* 25 -31	-4 213-234	2 215-196	-6 156-151	K=L= 1 4	-4* 43 56	3 88 -97	K=L= 6 6	K=L= 0 8	
4 81 81	-3 75 88	3* 43 -36	-5 288 289	-14* 41 -21	-3 83 -81	6* 37 27	-9 66 -82	-14 92 -86	
5* 23 35	-1 193 207	4 194-194	-4 204-217	-12* 32 -35	-2 65 -67	K=L= 7 5	-5 66 60	-13 51 47	
6* 36 45	0 53 47	5 204 202	-3 131-137	-10* 47 41	0 77 77	-5 54 60	-2* 44 43	-12 80 -90	
7 59 -62	1 65 -70	6 234 247	-2 99 -98	-9* 39 27	1 64 55	-1* 43 -49	-1 98 -86	-11 242 240	
8* 29 -35	2 80 79	7 98-102	-1 253-218	-8 105-108	2* 47 -45	0 87 89	0 72 82	-10 117-111	
9 72 69	3 115-113	8 97 -94	0 156 140	-2 144-128	3 64 -56	1* 47 -29	3 65 67	-9 223-215	
11* 29 -6	4 72 65	11 82 76	1 157-135	-1 198-183	5* 45 24	2* 33 -15	4 79 -88	-8 150 137	
12* 25 -29	5 93 100	12* 26 -22	2 77 -71	0* 34 -53	K=L= 1 5	3 68 58	7* 40 -11	-7 82 82	
K=L= 5 0	6 125-129	K=L= 3 2	3 318 306	1 318 294	-14 100 90	4 70 -56	K=L= 7 6	-6 178 189	
1 157-166	7* 22 22	-12* 35 -45	4 119-116	2 165-178	-13* 39 49	K=L= 0 6	-6 94 -85	-4 247-249	
2* 21 27	8* 23 -13	-11* 46 59	5 144 139	3 265 260	-12* 36 60	-14* 42 -37	-4* 39 58	-3 165 179	
3 74 -73	10 60 58	-10 120 134	6 174-182	4 80 66	-11* 41 -15	-13 58 66	-3* 33 -9	-2 158 122	
4 75 79	11 77 -68	-9 60 -61	7 139-132	6* 26 -12	-10 175-166	-12 97 92	-2* 34 -51	-1 75 87	
5* 26 22	K=L= 5 1	-8* 43 37	8* 37 43	7 65 -69	-9 154 153	-11 113 111	1 83 90	1 148-169	
6 98-106	-11* 26 33	-7 73 -77	10 90 82	8* 46 49	-8* 27 25	-10 262-254	K=L= 1 7	2 165 171	
8* 32 -39	-10* 29 -39	-6* 48 13	12* 32 -34	11 60 60	-7 77 -78	-8 92 93	-11 162 169	3 79 96	
9 71 76	-9* 45 27	-5 200 217	K=L= 3 3	12 72 -58	-6 82 -90	-7 105-100	-10 144-143	4 56 65	
11 76 -65	-7* 25 -41	-4 305-319	-11 58 -56	K=L= 2 4	-5* 27 -68	-6 131-124	-9 80 -68	5 174-127	
K=L= 6 0	-6 59 62	-3 80 -80	-9 100 103	-11 84 -96	-4 138 156	-5 142-136	-8 135 140	6 131-144	
0 110 -98	-5* 29 -41	-1 135 124	-8* 37 -18	-10 66 -70	-3 165 175	-4 60 42	-7* 29 7	8 52 38	
1 114 119	-4 60 73	0 248 236	-7 62 -62	-9 136 144	-2 106-102	-3 232 244	-5 197-196	10* 36 -9	
2 51 -56	-2 100-111	1 132-123	-6 102-110	-8* 28 23	0 224-209	-2 54 -50	-4 116-119	K=L= 1 8	
3 65 -61	1* 34 20	2 51 -55	-4 72 86	-7 59 63	1 229 233	-1 101 100	-3 272 279	-12 80 64	
4* 29 38	2 59 -54	3 123 115	-3 163 164	-6 223-218	2* 45 -2	0 343-344	-2* 42 -37	-10* 39 -33	
5* 24 -9	3 61 -70	5 93 96	-2 124 116	-5* 49 -63	3 82 -81	2 247 268	0 90 -90	-9 85 84	
6* 37 19	4* 45 55	6 179-182	-1 97 -98	-4 224 241	5 197-197	4 97 -91	1 120-126	-8* 43 -25	
8* 31 -26	5* 32 -30	7 100 -99	0* 49 -61	-3* 31 -18	6 56 69	5 149-170	2 189 188	-5 153-151	
9 54 61	6* 27 29	9* 36 -22	1 136 126	-2 74 73	7 101 97	7 98 102	4* 47 43	-4 83 74	
K=L= 7 0	10 50 34	10 104 94	3 70 -68	-1 128 -95	8 96-102	9* 40 6	5* 46 -36	-3 102 -88	
2* 27 -16	K=L= 6 1	11 64 -51	4 96 -96	0 97-104	10 52 -36	K=L= 1 6	6 100 -97	-2 228 220	
3* 46 49	-9 72 -68	K=L= 4 2	6 164 165	1 234 212	11 62 43	-14* 39 -13	7 128 137	0 121-124	
4 85 92	-6* 37 38	-10* 36 -28	8 92 -86	2 141-122	12* 47 29	-12* 33 52	8 62 43	1 52 60	
6* 39 -45	-5 57 63	-9 61 65	10* 47 -63	3 64 70	K=L= 2 5	-11 58 -36	K=L= 2 7	2 59 85	
K=L= 8 0	-4 79 -98	-7 110-127	11* 37 32	4 264-260	-13* 39 -38	-8 77 -81	-12 55 37	3* 31 25	
0 72 -69	0 58 58	-4 134 147	K=L= 4 3	5* 47 -50	-11 85 -69	-5 57 -47	-9 74 76	9* 41 20	
1* 32 27	1 109-103	-3 186 205	-10 161 166	6 238 246	-9* 46 55	-4 74 60	-8 79 -80	K=L= 2 8	
K=L= 1 1	4* 37 39	-2* 46 -52	-9* 42 -19	7* 34 40	-8 88 -76	-2 85 83	-6* 50 -43	-9 127-109	
-12* 44 -33	5* 33 30	-1 112-105	-7 54 -56	8 82 -89	-7 144 129	-1 66 -73	-5 193-190	-8 85 92	
-11* 36 -40	6* 49 -54	0* 34 24	-6 113-126	9* 36 -12	-6 165-142	1 72 88	-4 169 164	-6 105 96	
-10 174 174	8* 34 -18	1 53 49	-5 185 202	10* 29 -36	-5 223 216	2* 26 -28	-2 84 60	-5* 36 -46	
-8 98 102	K=L= 7 1	2* 25 13	-4 124-141	11 58 60	-4 181 180	6* 47 -49	-1 74 -62	-4 318-301	
-7* 37 -44	-6 63 79	3 94-105	-3 155-165	K=L= 3 4	-3* 34 -55	K=L= 2 6	0 144-139	-3 266 251	
-6 69 -81	-4* 39 17	4* 29 41	-2* 33 -27	-12* 37 -32	-2 120 112	-13* 41 38	1 74 77	-2 126 109	
-5 141 143	-2 82 -95	6 84 85	0 238 232	-11 95 -92	-1 120-138	-12 59 44	2* 30 -21	-1 163-147	
-4 125-127	-1 122 117	8* 41 -31	1 95 -80	-10 118 122	1 83 92	-11 56 48	3 104-109	1 172-175	
-3 191-217	0 95 -97	10* 39 45	2 102 -95	-7 85 87	2 148-143	-10 150-162	4 95 104	2 123 119	
-2 168-183	1* 43 42	11* 34 20	4* 28 3	-6 250-267	3 165 166	-8 154 155	5 108-112	3 84 81	
-1 267-278	2* 39 30	K=L= 5 2	5 148 138	-5 335 342	4* 42 -32	-5 334-326	K=L= 3 7	5 59 -56	
0 737 688	3 67 -61	-10 89 102	6* 33 22	-3 189-177	5 67 -65	-4 52 56	-13* 41 -1	6 108-120	
1 210 207	4* 34 54	-9* 43 -35	7 74 -69	-2 80 80	6 114 106	-3 413 372	-10 81 -82	7 86 81	
2 51 -38	5* 46 -34	-7 72 -86	8* 30 33	-1 204-207	7 122-121	-2 105 -88	-9* 39 -18	8 81 67	
3 190-192	6* 38 -36	-5 112 118	10 60 60	0 118 107	8* 34 21	-1 65 -66	-8 135 132	9 55 -28	
4 251-243	K=L= 8 1	-4 115-131	K=L= 5 3	1 68 88	9* 40 4	0 273-259	-7* 43 38	10 62 -29	
5 264 275	-3 80 -96	-3 64 -61	-11* 50 33	2 158-139	11* 44 38	1 51 -41	-5 172-163	K=L= 3 8	
6 67 68	-2* 29 35	-2* 29 24	-9* 46 67	4* 44 46	K=L= 5 5	2 60 58	-4 62 49	-10 69 -72	
7 278-271	0* 38 -30	-1* 42 38	-7 103-118	5 90 90	-11 76 -70	3 128 119	-3 180 194	-9 84 71	
9 56 -47	2* 47 -52	0 233 217	-6* 37 25	6 63 58	-10 101-117	4* 34 11	-2 131 123	-8 53 25	
10 68 70	K=L= 0 2	1 151-134	-5* 38 -54	7 142-136	-9* 35 46	5 139-136	-1 74 -67	-7 90 -92	
11 70 68	-14* 38 42	2 116-114	-4* 50 -49	8 63 63	-8 148 157	6 102 104	0 145-138	-5 147-153	
12 92 -84	-11 162-154	3* 27 34	-3 102 114	10 68 64	-7 87 -72	7 119 126	1* 37 -45	-4 128 126	
K=L= 2 1	-10 151 144	4* 32 -33	-2* 26 -41	K=L= 4 4	-6 79 -87	8* 41 -46	3 62 51	-3 96 106	
-13* 29 0	-9 104 103	5 125 124	0* 39 31	-11 56 -50	-5 56 -57	9* 48 -47	4* 44 -36	-2 75 -87	
-12* 34 -30	-7 54 -54	6* 50 -48	2 152 131	-9 77 79	-4 126 117	10 64 -55	5 62 -61	0 133-125	



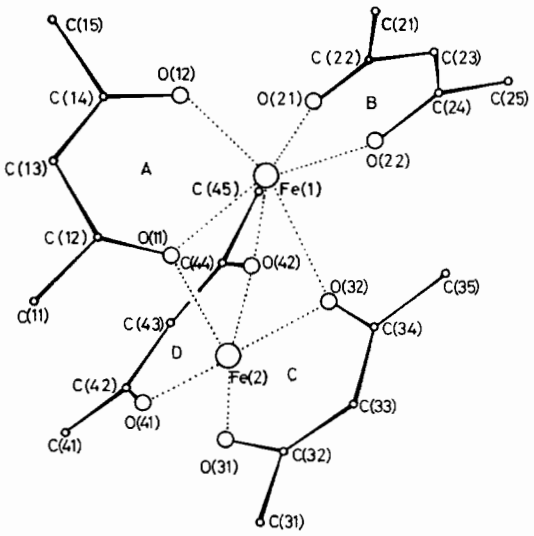


Figure 1. Projection of the molecular skeleton along the *b*-axis.

The average angle of O_{ax}–Fe–O_{eq} is 90° (73–107°). The out of plane distance of the Fe(1) atom is 0.21 Å toward O(21). The polyhedron about Fe(2) may be described as a distorted square pyramid having O(31), O(32), O(41) and O(42) at the base plane and O(11) at the apex. The average O_{apex}–Fe–O_{base} angle is 90° (77–104°) and Fe(2) atom lies 0.06 Å above the basal plane of oxygen atoms.

The deviations of atoms from the least-squares planes of the four chelate rings are listed in Table VI. The values are reasonable as compared with those of other metal acetylacetonates [8]. The dihedral angles of the planes for A/B and C/D are 79° and 25°, respectively.

The two ferrous ions are bridged by three oxygen atoms, O(11), O(32) and O(42), and the octahedron and square pyramid share a common face made by these oxygen atoms. A schematic drawing illustrating the coordination polyhedra is given in Figure 2. The structure recalls that formed by fusion of an octahedron and a pentahedron in zinc acetylacetonate [4], though in that case the zinc atoms are bridged by only two oxygens. The structure of the iron complex is rather similar to that of nickel acetylacetonate [2] because it would arise from degradation of the trimeric nickel complex to a dimer through removal of a terminal $Ni(acac)_2$.

In oligomers such as the cobalt, nickel and zinc acetylacetonate complexes, metal–metal distances can be roughly classified into two groups. The distance between metal atoms bridged by oxygens on a common face is 2.89 Å for the nickel complex and 3.19 Å for the cobalt complex, while the distance between the metals bridged by oxygens on a common edge are longer, 3.57 Å for the cobalt complex, and

TABLE IV. Bond Lengths and Their Standard Deviations (Å).

O(11) C(12)	1.27(3)	C(12) C(13)	1.42(3)	C(11) C(12)	1.56(3)
O(12) C(14)	1.27(3)	C(13) C(14)	1.40(3)	C(14) C(15)	1.56(3)
O(21) C(22)	1.28(2)	C(22) C(23)	1.41(3)	C(21) C(22)	1.55(3)
O(22) C(24)	1.34(3)	C(23) C(24)	1.34(4)	C(24) C(25)	1.55(4)
O(31) C(32)	1.27(3)	C(32) C(33)	1.40(3)	C(31) C(32)	1.51(3)
O(32) C(34)	1.35(3)	C(33) C(34)	1.39(2)	C(34) C(35)	1.49(3)
O(41) C(42)	1.30(3)	C(42) C(43)	1.41(3)	C(41) C(42)	1.49(3)
O(42) C(44)	1.33(3)	C(43) C(44)	1.38(3)	C(44) C(45)	1.54(3)
mean	1.30	mean	1.39	mean	1.53
Fe(1) O(11)	2.08(1)	O(11) O(12)	2.81(2)	O(31) O(41)	3.14(2)
Fe(1) O(12)	2.04(2)	O(21) O(22)	2.83(2)	O(11) O(31)	3.22(2)
Fe(1) O(21)	2.04(2)	O(31) O(32)	2.81(2)	O(11) O(41)	3.27(2)
Fe(1) O(22)	2.02(1)	O(41) O(42)	2.77(2)		
Fe(2) O(31)	2.00(1)	O(12) O(22)	3.28(2)		
Fe(2) O(32)	2.07(1)	O(22) O(32)	3.12(2)		
Fe(2) O(41)	2.00(2)	O(11) O(32)	2.63(2)		
Fe(2) O(42)	2.06(1)	O(21) O(11)	3.31(2)		
mean	2.04	O(21) O(12)	2.97(2)	Fe(1) Fe(2)	3.028(3)
		O(21) O(32)	3.31(2)		
Fe(1) O(32)	2.33(1)	O(42) O(11)	2.65(2)		
Fe(1) O(42)	2.27(1)	O(42) O(12)	3.22(2)		
Fe(2) O(11)	2.15(1)	O(42) O(22)	2.99(2)		
		O(42) O(32)	2.73(2)		

TABLE V. Bond Angles and Their Standard Deviations (°).

Fe(1) O(11) C(12)	129(1)	O(11)	C(12)	C(13)	127(2)
Fe(1) O(12) C(14)	127(1)	O(12)	C(14)	C(13)	130(2)
Fe(1) O(21) C(22)	128(1)	O(21)	C(22)	C(23)	125(2)
Fe(1) O(22) C(24)	126(1)	O(22)	C(24)	C(23)	127(2)
Fe(2) O(31) C(32)	130(1)	O(31)	C(32)	C(33)	124(2)
Fe(2) O(32) C(34)	130(1)	O(32)	C(34)	C(33)	118(2)
Fe(2) O(41) C(42)	132(1)	O(41)	C(42)	C(43)	122(2)
Fe(2) O(42) C(44)	129(1)	O(42)	C(44)	C(43)	122(2)
mean	129		mean		124
C(11) C(12) C(13)	115(2)	O(11)	C(12)	C(11)	118(2)
C(13) C(14) C(15)	116(2)	O(12)	C(14)	C(15)	114(2)
C(21) C(22) C(23)	117(2)	O(21)	C(22)	C(21)	118(2)
C(23) C(24) C(25)	124(2)	O(22)	C(24)	C(25)	109(2)
C(31) C(32) C(33)	121(2)	O(31)	C(32)	C(31)	115(2)
C(33) C(34) C(35)	126(2)	O(32)	C(34)	C(35)	116(2)
C(41) C(42) C(43)	121(2)	O(41)	C(42)	C(41)	118(2)
C(43) C(44) C(45)	123(2)	O(42)	C(44)	C(45)	114(2)
mean	120		mean		115
O(11) Fe(1) O(12)	85.9(6)	C(12)	C(13)	C(14)	120(2)
O(21) Fe(1) O(22)	88.4(6)	C(22)	C(23)	C(24)	125(2)
O(31) Fe(2) O(32)	87.3(5)	C(32)	C(33)	C(34)	130(2)
O(41) Fe(2) O(42)	86.1(6)	C(42)	C(43)	C(44)	127(2)
mean	86.9		mean		126

3.259 Å for the zinc complex. The metal–metal distance in the iron complex is 3.028 Å and belongs to the first type.

There are two significantly different types of iron to oxygen bond. The first is the bond between an iron atom and the oxygen atom of its chelating

TABLE VI. Deviations of Atoms from the Least-squares Plane through Five Atoms ($OC_cC_sC_cO$).

Deviations (Å)				
	A	B	C	D
O_1[a]	0.023	0.023	0.000	0.002
O_2	−0.015	−0.025	0.011	0.023
C_2	−0.031	−0.028	−0.024	−0.018
C_3	0.011	0.000	0.047	0.042
C_4	0.011	0.029	−0.036	−0.046
C_1	−0.152	0.000	−0.136	−0.081
C_5	0.023	0.054	−0.139	−0.144
Fe(1)	0.288	−0.101	−1.188	−1.095
Fe(2)	−1.278	1.636	0.246	0.290

Equations of the Planes: $du + ev + fw + g = 0$[b]

	A	B	C	D
d	−0.3936	0.7434	0.5366	0.6011
e	0.8963	0.4258	−0.6353	−0.2645
f	0.2043	0.5158	0.5554	0.7541
g	−4.4974	−6.5465	−3.5651	−6.5652

[a]Subscripts refer to the last digit of the numbering system shown in Figure 1. [b]u, v and w are the orthogonal coordinates (Å) defined by $u = ax + cz\cos\beta$, $v = by$, $w = cz\sin\beta$.

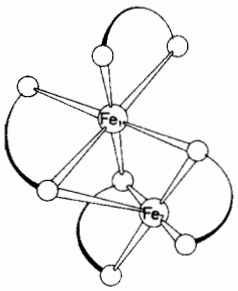


Figure 2. Schematic drawing illustrating the coordination polyhedra.

TABLE VII. Comparison of Some Parameters of Acetylacetone Groups.

	Fe[a]	Co[b]	Ni[c]	Zn[d]	M(acac)$_n$[e]
O–C_c	1.30 Å	1.28 Å	1.33 Å	1.274 Å	1.28 Å
C_c–C_s	1.39	1.47	1.55	1.386	1.40
C_c–C_m	1.53	1.57	1.53	1.506	1.52
O C_c C_s	124°	123°	125°	125.2°	125°
C_c C_s C_c	126	127	118	126.3	125
O C_c C_m	115	117	118	116.1	116

[a]Present study. [b]Ref. 3. [c]Ref. 2. [d]Ref. 4. [e]Ref. 8.

TABLE VIII. Intermolecular Contacts.

C(31)	C(44)[i]	3.63 Å
C(32)	C(34)[i]	3.52
C(33)	C(42)[i]	3.84
C(21)	C(45)[ii]	3.46
C(21)	C(45)[iii]	3.85

none	x,	y,	z
i	1 − x,	1 − y,	1 − z
ii	x,	1/2 − y,	1/2 + z
iii	x,	1 + y,	z

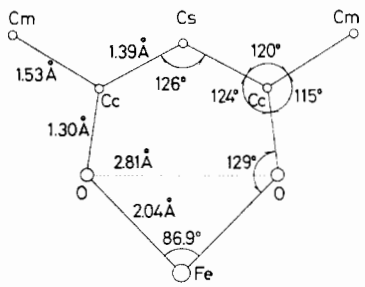


Figure 3. Mean values of bond lengths (Å) and angles (°) of the chelate ring.

ligand, irrespective of whether the oxygen is bridging or not. The average bond length for this type is 2.04 Å. The second is the bond between an iron atom and the oxygen atom of a ligand chelating the other iron atom. The three bond lengths for the second type have values 2.15, 2.27 and 2.33 Å, which are all greater than the values for the first type.

The distances between adjacent oxygen atoms can be classified into three groups. The average distance of the bite O–O is 2.81 Å and that of a non-bite pair is 3.18 Å. The third group comprises O–O pairs in the common face of the polyhedra, for which the average distance is very short, 2.67 Å.

Anderson and coworkers [9] have recently reported that in ferrous chlorophosphate, each iron atom is coordinated by four oxygen atoms and two chlorine atoms in *trans* positions, and the three octahedra are fused by sharing adjacent faces of the central octahedron. The Fe–O distances are grouped into three types with average distances of 1.927, 2.080 and 2.241 Å as a result of the bonding scheme. The average shortest Fe–Fe distance is 3.063 Å, which is close to that now found in ferrous acetylacetonate.

Average values for chemically equivalent bond lengths and angles of ferrous acetylacetonate are shown in Figure 3, and in Table VII some of these values are compared with these of other metal acetylacetonates. As seen from this Table, the parameters from the present study are in good agreement

with those obtained hitherto on other acetylacetonates.

Some close intermolecular contacts are found between the methyl–methyl and methyl–methylene carbon atoms. They are given in Table VIII. Other intermolecular distances can be explained reasonably by the assumption that they represent van der Waals contacts.

Acknowledgement

The authors wish to thank Dr. S. Utsuno for his advice on the preparation of ferrous acetylacetonate.

References

1 S. Shibata, *Bull. Chem. Soc. Japan, 30,* 753 (1957).
2 G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem., 4,* 456 (1965).
3 F. A. Cotton and R. C. Elder, *ibid., 4,* 1145 (1965).
4 M. J. Bennett, F. A. Cotton and R. Eiss, *Acta Cryst., B24,* 904 (1968).
5 D. A. Buckingham, R. C. Gorges, and J. T. Henry, *Aust. J. Chem., 20,* 281 (1967).
6 "International Tables for X-ray Crystallography", Vol. III, Kynoch Press, Birmingham (1962).
7 "The Universal Crystallographic Computing System (I)", The Crystallographic Society of Japan, Tokyo (1967).
8 E. C. Lingafelter, *Coord. Chem. Rev., 1,* 151 (1966).
9 J. B. Anderson, J. R. Rea and E. Kostiner, *Acta Cryst., B32,* 2427 (1976).