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Crystallographic data for some ferrocene derivatives.

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Bis(cyclopentadienyl)iron(II) compounds, better known as ferrocenes, have been the subject of numerous publications in the last few years. Ferrocene itself was discovered only twelve years ago (Kealy & Pauson, 1951) and its structure has been investigated but the results do not all agree (Eiland & Pepinsky, 1952; Dunitz, Orgel & Rich, 1956). The present author's data agree with those published by Dunitz *et al.* Crystal data for ferrocene derivatives have been published in only a few cases (Struchkov, 1956; Struchkov & Khotsyanova, 1958). Table 1 lists the crystal data for fourteen different ferrocene derivatives as determined by the author.

The lattice parameters were obtained from Weissenberg and precession photographs with Mo $K\alpha$ radiation.

Space groups were determined from systematic absence except for $A2/a$ and $C2/m$ which were chosen because of the eight equivalent positions.

Flotation density measurements were made where possible in a mixture of carbon tetrachloride and petroleum ether and are denoted by D_m in the table. Densities calculated from the X-ray data are listed under D_x.

The purity of each crystal was checked by its melting point range.

X-ray powder patterns were made of each compound and all the powder lines could be easily indexed from the crystal data in the table.

References

Dunitz, J. D., Orgel, L. E. & Rich, A. (1956). *Acta Cryst.* **9**, 373.

Eiland, P. F. & Pepinsky, R. (1952) *J. Amer. Chem. Soc.* **74**, 4971.

Kealy, T. J. & Pauson, P. L. (1951). *Nature, Lond.* **168**, 1039.

Struchkov, Y. T. (1956). *Doklady Akad. Nauk* SSSR, **110**, 67.

Struchkov, Y. T. & Khotsyanova, T. L. (1958). *Kristallografiya*, **2**, 382.

Table 1. *Crystallographic data for ferrocene derivatives*

Compound	a	b	c	β	S.G.	Z	D_m	D_x	m.p.
Ferrocene	10·56 Å	7·597 Å	5·952 Å	121°	$P2_1/a$	2		1·516	
Ethyl ferrocenoate	5·89	11·13	17·91		$P2_12_12_1$	4		1·454	63·0– 64·0 °C
Phenyl ferrocenoate	9·69	10·43	13·54	94° 25′	$P2_1/c$	4	1·482	1·489	124·0–124·5
Benzoylferrocene	13·93	15·19	6·20	99° 40′	$P2_1/n$	4	1·507	1·484	107·8–108·3
1,1′-Dibenzoylferrocene	11·60	25·20	6·28	90° 05′	$P2_1/n$	4	1·420	1·429	104·0–105·0
Benzoylferrocene oxime	7·56	20·59	8·88		$P2_12_12_1$	4		1·462	161·0–162·5
2,4-Dimethoxybenzoylferrocene	7·77	24·26	8·40		$P2_12_12_1$	4	1·445	1·429	132·5–133·5
2,4-Dihydroxybenzoylferrocene	8·41	24·16	13·85		$Pna2$	8	1·523	1·515	176·0–177·0
O-Hydroxybenzoylferrocene	6·14	19·75	11·12		$P2_12_12_1$	4	1·512	1·502	87·5– 88·5
2-Hydroxy-4-methoxybenzoylferrocene	7·42	13·42	14·54	93° 05′	$P2_1/n$	4	1·562	1·540	124·0–125·5
1,1′-Bis(α-hydroxyethyl)-ferrocene	6·13	16·52	12·72	95° 25′	$P2_1/c$	4	1·412	1·420	69·0– 71·0
1,1′-Hydroxymethylferrocene	10·45	7·72	13·36	105° 40′	$P2_1/a$	4		1·575	104·0–105·0
Dimethyl 1,1′-ferrocene-dicarboxylate	13·34	5·96	32·67	104° 20′	$A2/a$	8	1·589	1·594	113·5–114·5
1,1′-Bis(*p*-fluorobenzoyl)ferrocene	12·69	21·11	13·65	91° 45′	$C2/m$	8	1·560	1·564	129·0–130·5
Di(2,3-epoxypropyl) 1,1′-ferrocenedicarboxylate	11·94	5·96	23·88	102°	$P2_1/c$	4		1·543	51·5– 52·5

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Crystal data for dioctadecyl adipate, $C_{42}H_{82}O_4$.

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In soft X-ray spectroscopy there is a great deal of interest in finding a crystal which will disperse X-rays of wavelengths between about 25 and 100Å. Most investigators who do not like the ruled diffraction grating method are turning to artificially fabricated 'crystals' which are built up of many monolayers of a soap film such as barium stearate. This so-called crystal has a $2d$ spacing of approximately 100Å but the monolayer films are rather difficult to make and usually do not give the intensity or peak-to-background ratio which one usually desires. Many attempts have been made to grow organic single crystals with large $2d$ spacings but obstacles such as poor crystal growth, instability in air or vacuum, very low melting point, absence of desired reflections or poor diffracting qualities usually preclude their practical use.

One such crystal which appears to overcome these difficulties, however, is dioctadecyl adipate,

$$CH_3(CH_2)_{17}OOC(CH_2)_4COO(CH_2)_{17}CH_3.$$

Excellent single crystals can be grown in benzene.

Small crystals were subjected to X-ray analysis and the unit-cell dimensions were determined from Weissenberg and precession photographs with Cu $K\alpha$ radiation. The cell is monoclinic with

$$a = 44{\cdot}45,\ b = 7{\cdot}414,\ c = 94{\cdot}76\text{Å},\ \beta = 107\ °20'.$$

Systematic absences and optical examination show that it belongs to space group $A2/a$ or Aa. The density was measured by the flotation method in a mixture of water and methanol and found to be 0·883 g.cm^{-3}. This density corresponds to 24 molecules per cell. The melting point is 64 °C.

The maximum usable $2d$ spacing of the crystal is 90·55Å (002 plane) and the reflections are fairly strong. Fortunately, the crystals grow in platelet form with the large face parallel to the 90Å spacing.

Dioctadecyl adipate gives a rather poor powder pattern and the large cell dimensions make it quite difficult to assign all possible indices to each powder line. There were, however, about twenty spots on the single-crystal photographs which were much more intense than the rest of the spots and these were used to index the powder pattern as is shown in Table 1. The pattern was taken with a 2-radian Debye–Scherrer camera and Cu $K\alpha$ radiation.

Table 1. *Indexed powder pattern for* $C_{42}H_{82}O_4$

d	I/I_1	hkl
14·9 Å	1	006
11·3	<1	008
9·06	<1	0,0,10
4·13	100	717
3·70	30	020
3·23	1	0,0,28
2·48	5	$14,0,\overline{14}$
2·22	5	$18,0,\overline{30}$
1·99	10	$4,0,\overline{42}$
1·72	5	$25,1,\overline{23}$

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References

Müller, A. & Lonsdale, K. (1948). *Acta Cryst.* **1**, 129.

Ruderman, W., Losin, E. & Uphoff, D. (1963). ASD TDR 63-311.

Sydow, E. von (1955). *Acta Cryst.* **8**, 557.

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Gadolinium and dysprosium intermetallic phases. III. The structures of Gd_3Al_2, Dy_3Al_2, Gd_5Ge_3, Dy_5Ge_3 and $DyAl_3$.

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The structures of Dy_3Al_{12} and Gd_3Al_2 were determined by single-crystal X-ray diffraction techniques. Single-crystal chips from arc-melted alloys (for preparation, see Baenziger & Moriarty, 1961) were mounted and aligned on Buerger precession cameras. The tetragonal cell constants are for Gd_3Al_2:

$$a = 8{\cdot}344 \pm 0{\cdot}004,\ c = 7{\cdot}656 \pm 0{\cdot}006\ \text{Å},\ Z = 4;$$

for Dy_3Al_2:

$$a = 8{\cdot}164 \pm 0{\cdot}005,\ c = 7{\cdot}560 \pm 0{\cdot}007\ \text{Å},\ Z = 4.$$

Possible space groups are $P4_2nm$, $P\bar{4}n2$, $P4_2/mnm$.

Since the smallest and most perfect alloy fragment found was from a Gd_3Al_2 alloy, the intensity data were collected from this crystal. Precession data ($0kl$ to $3kl$) and Weissenberg ($hk0$) were collected and estimated by visual comparison with a calibrated intensity strip. The data were corrected by Lorentz and polarization factors, but not for absorption. Patterson maps calculated from the ($hk0$) and ($0kl$) data suggested that the structure was similar to that reported by Edshammar (1962) for Hf_3Al_2. (Edshammar determined this structure from powder data but did not report any parameters, only a projection of the structure.) Trial structures in space groups $P\bar{4}n2$ and $P4_2/mnm$ using the Patterson parameters for Gd did not refine below $R = 39\%$. The trial structure in $P4_2nm$ refined in five cycles of least-squares to $R = 12{\cdot}2\%$ including absent reflections ($R = 10{\cdot}6\%$ for present reflections only).

The final atomic positions are:

4 Gd(1) in (c):
$x, x, z;\ \bar{x}, \bar{x}, z;\ \frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}+z;$
$\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2}+z;$ with $x = 0{\cdot}152 \pm 0{\cdot}0006$,
$z = 0{\cdot}268 \pm 0{\cdot}0008$, $B = 1{\cdot}55$ Å^2.

4 Gd(2) in (c):
with $x = 0{\cdot}205 \pm 0{\cdot}0006$, $z = 0{\cdot}742 \pm 0{\cdot}0008$,
$B = 1{\cdot}65$ Å^2.

4 Gd(3) in (b):
$0, \frac{1}{2}, z;\ \frac{1}{2}, 0, z;\ 0, \frac{1}{2}, \frac{1}{2}+z;\ \frac{1}{2}, 0, \frac{1}{2}+z;$ with
$z = 0{\cdot}517 \pm 0{\cdot}0008$, $B = 1{\cdot}75$ Å^2.

4 Al(1) in (c):
with $x = 0{\cdot}377 \pm 0{\cdot}001$, $z = 0{\cdot}048 \pm 0{\cdot}002$, $B = 1{\cdot}97$ Å^2.

4 Al(2) in (c):
with $x = 0{\cdot}396 \pm 0{\cdot}001$, $z = 0{\cdot}456 \pm 0{\cdot}002$, $B = 1{\cdot}97$ Å^2.

The interatomic distances based on these positions are:

Gd(1) has
1 Al(1) at 3·14 Å, 2 Al(1) at 3·15, 1 Al(2) at 3·22,
1 Al(2) at 3·23, 1 Gd(1) at 3·58, and 1 Gd(2) at
3·69 Å.