

complete on the sub-units and a set complete on the gaps, both sets vanishing on the sub-unit boundaries. Clearly the original set of functions can give non-zero densities on the sub-unit boundaries. In one dimension, where the boundaries are points, this distinction is not important. In two- and three-dimensions where the boundaries become respectively closed curves and surfaces, the effect is significant and means that the observed gradient of the (m, N) plots for two- and three-dimensional examples is always less than $(2U/V)$.

Most of the material described in this paper is taken from a Ph.D. thesis submitted to Cambridge Univer-

sity. The author is grateful to Dr D.M. Blow for helpful discussions during the preparation of this manuscript. The work was undertaken while the author was holder of a Medical Research Council Scholarship.

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The Crystal Structure of Tris(cyclopentadienyl)samarium (III).*

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(Received 5 February 1969 and in revised form 28 April 1969)

The crystal structure of tris(cyclopentadienyl)samarium (III), $\text{Sm}(\text{C}_5\text{H}_5)_3$, has been determined by analysis of three-dimensional X-ray diffraction data. The crystals are orthorhombic, space group $Pbcm$, with eight chemical formula units per unit cell. Cell dimensions are: $a = 14.23$, $b = 17.40$ and $c = 9.73$ Å. The heavy atom positions were deduced from Patterson projections, and cyclopentadienyl rings were found from difference syntheses. The final R value for the 1266 observed reflexions is 12.5%. The eight $\text{Sm}(\text{C}_5\text{H}_5)_3$ in the unit cell are divided into two symmetrically independent, and structurally different groups (A and B). The A and B groups form close-packed infinite chains along the c axis and the A and B chains alternate in layers parallel to (100) with an average spacing of $\frac{1}{2}a$. In either group, the samarium atom could be described as having a distorted tetrahedral environment and approximately three pairs of electrons are responsible for the bonding between the metal atom and the cyclopentadienyl rings. Both types of structures are disordered, and a plausible mechanism for the disorder is discussed.

Introduction

This paper deals with the crystal structure determination of tris(cyclopentadienyl)samarium(III), $\text{Sm}(\text{C}_5\text{H}_5)_3$. The present work is the second of a series on the study of metal-cyclopentadienyls (Wong, Yen, & Lee, 1965), and $\text{Sm}(\text{C}_5\text{H}_5)_3$ is the first rare earth tris(cyclopentadienyl) complex ever to be studied.

This compound has been reported as having a pure electrostatic type of bonding (Birmingham & Wilkinson, 1956). However, in view of the much darker colour of the compound in its crystalline state (orange red) as compared with the samarium ion (light yellow), and the low sublimation temperature ($\sim 160^\circ\text{C}$ in vacuum), we suspect that the bonding may be somewhat covalent. Also, there exists almost no structural information concerning bonding between rare earth metal

and organo-carbon atoms. For the above reasons, we feel that careful structural study of this compound is of interest.

Experimental

The air and moisture sensitive compound was synthesized in this laboratory according to Birmingham & Wilkinson (1956). The single crystals used were grown by sublimation at $\sim 160^\circ\text{C}$ under reduced pressure in thin-walled Pyrex capillaries. Laue photographs showed it to be of mmm symmetry; zero-layer Weissenberg photographs taken along the three principal axes, with $\text{Mo } K\alpha$ radiation, showed the following systematic absences: $h00$ for h odd, $0kl$ for k odd and $h0l$ for l odd, which would make the space groups $Pbcm$ or $Pbc2_1$, most probable. However, in either case the extinction condition $h00$ for h odd had to be considered as incidental. The centrosymmetric space group $Pbcm$ was tentatively chosen, and it was later shown to be correct. For data collection, the equi-inclination, multiple-film Weissenberg technique was used with Zr-filtered $\text{Mo } K\alpha$ radiation. Copper foils were inserted be-

* Presented at the Tenth International Conference on Coordination Chemistry, Nikko, Japan, 1967.

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Table 1. *The final parameters and their estimated standard deviations*

The samarium parameters have been multiplied by a factor of 10^5 , and those of carbon by 10^3 . The isotropic temperature factor $B=10$ has been assigned to *A*III and *B*III. The quoted e.s.d.'s for *A*I, *A*II, *B*I, and *B*II are obtained from conditioned least squares as described in the text. The anisotropic temperature factor is in the form

$$T = \exp [-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + hk B_{12})].$$

	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>B</i> ₁₁	<i>B</i> ₁₂	<i>B</i> ₃₃	<i>B</i> ₁₂
Sm(<i>A</i>)	-549 (8)	16193 (10)	$\frac{3}{4}$	136 (4)	130 (4)	400 (11)	—
Sm(<i>B</i>)	50001 (18)	41184 (19)	$\frac{3}{4}$	571 (13)	413 (11)	1620 (38)	—
C(1) } <i>A</i> I	-195	142	677	12 (3)	14 (3)	34 (8)	-12 (4)
C(2) } (2)	-147	076	633				
C(3) } (2)	-117	035	$\frac{3}{4}$				
C(4) } (2)	184	142	677				
C(5) } <i>A</i> II	135	076	633	12 (3)	14 (3)	34 (8)	12 (4)
C(6) } (2)	106	035	$\frac{3}{4}$				
C(7) } (2)	-055	261	533				
C(8) } (2)	-086	301	652				
C(9) } <i>A</i> III	-005	325	725	11 (3)	16 (3)	25 (6)	-3 (4)
C(10) } (3)	075	301	652				
C(11) } (3)	044	261	533				
C(12) } (3)	312	389	677				
C(13) } <i>B</i> I	357	320	633	11 (3)	16 (3)	25 (6)	3 (4)
C(14) } (2)	384	278	$\frac{3}{4}$				
C(15) } (2)	688	389	677				
C(16) } <i>B</i> II	643	320	633				
C(17) } (3)	616	278	$\frac{3}{4}$	11 (3)	16 (3)	25 (6)	3 (4)
C(18) } (3)	420	509	528				
C(19) } (3)	451	549	649				
C(20) } <i>B</i> III	549	549	649				
C(21) } (3)	580	509	528	11 (3)	16 (3)	25 (6)	3 (4)
C(22) } (3)	500	485	455				

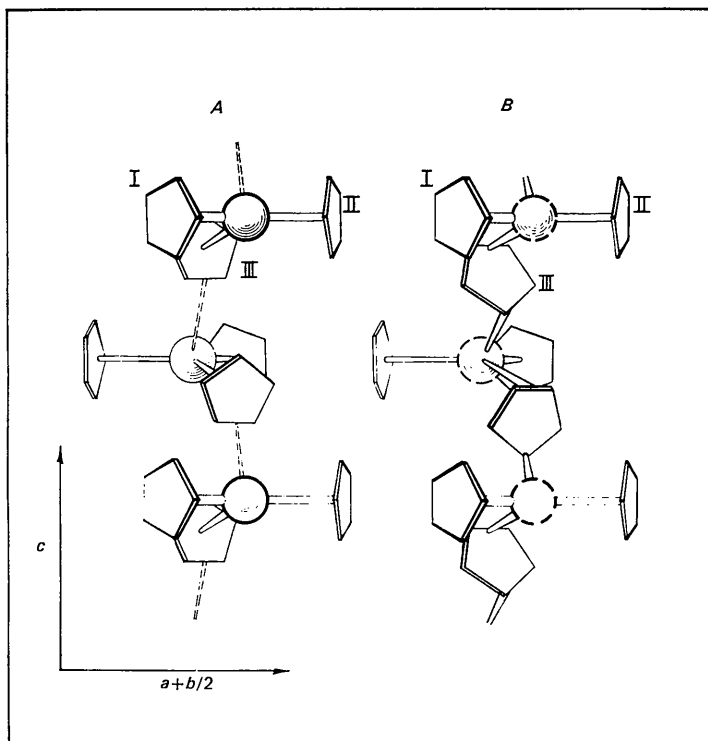


Fig. 1. A view of the *A* and *B* structures along the [120] direction, showing the difference between the two structures. Dashed circle for Sm(*B*) implies its diffuseness; dashed bonds indicate long bonds.

Table 2 (cont.)

11	10	9	8	7	6	5	4	3	2	1	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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metry-independent sets $(0, \frac{1}{2}, \frac{3}{4})$ for A , and $(\frac{1}{2}, \frac{5}{12}, \frac{3}{4})$ for B . A structure factor calculation with all the Mo data gave an R value of about 50%. Comparing carefully the calculated and observed structure factors, we discovered that for all the reflexions with $h+k/2$ even (about 800, and most of these were strong) reasonably good agreement was obtained ($R \sim 20\%$), whereas for the rest of them (all weak) the calculated values were much too weak as compared with the observed values. Four cycles of least-squares calculations with unit weights on the positional and isotropic thermal parameters of Sm for all the $h+\frac{1}{2}k$ even reflexions improved R to about 14%. However, the resulting temperature factor for Sm(A) was only one half of that for Sm(B). An $F_o - F_{sm}$ synthesis calculated with only the $h+\frac{1}{2}k$ even terms revealed cyclopentadienyl rings AI, AII, BI and BII (see Fig. 1 for identification). Spurious peaks up to 10 e.A⁻³ were found on and around the positions where rings AIII and BIII were expected to lie. Further calculations including the four rings improved but little the agreement for the reflexions with $h+\frac{1}{2}k$ even, and almost no improvement was achieved for the remaining reflexions. At this stage a thorough re-examination of the whole situation was made. The structure factors were shown to have the following three characteristic features. If we let F_A and F_B represent the contribution to the structure factors

from set A and set B respectively, then we have: (1) for $h+\frac{1}{2}k$ even, $F = F_A + F_B$, (2) for $h+\frac{1}{2}k$ odd, $F = F_A - F_B$, and (3) for k odd F is the difference between the contributions of the structure factors from the two subcells, $b=0$ to $b=\frac{1}{2}$, and $b=\frac{1}{2}$ to $b=1$. In order that the reflexions of class (2) are non-zero, either there should be defects in A or B , or A and B should be of two different atomic arrangements. Density measurement ruled out the first possibility, and we had to explore the second. To fit (3), a slight deviation from the structure deduced from the Patterson syntheses for Sm(A) ($x=0$) and Sm(B) ($x=\frac{1}{2}$) must be considered.

Full-matrix least-squares refinement was carried out on positional and anisotropic thermal parameters of samarium atoms only, using all the observed data. Weights used were those suggested by Hughes (1941). Three cycles later the R value for the complete data was 17%. However, for a considerable number of low order reflexions the agreement was still poor, and also the average thermal parameter of Sm(B) was about five times greater than that of Sm(A).^{*} A difference synthesis was calculated, and the results were still disappointing: only rings AI, AII, BI and BII could be

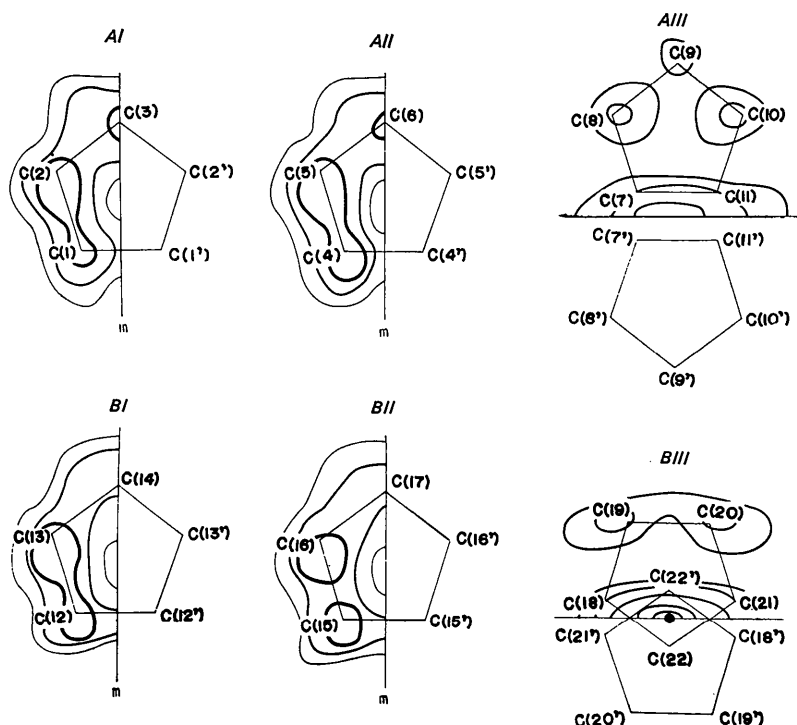
^{*} We tried the space group $Pbc2_1$, and placed the Sm atom initially slightly away from the mirror plane. However, this was shown to be incorrect.

Table 3. *Interatomic distances and angles*The e.s.d.'s of the distances have been multiplied by 10^2 and are given in brackets.

Sm(A)		Sm(B)	
C(3) } C(6) }	2.73 (3) Å	C(14) C(17)	2.85 (3) Å
C(2) } C(5) }	2.76 (3)	C(13) C(16)	2.83 (3)
C(1) } C(4) }	2.80 (3)	C(12) C(15)	2.80 (3)
(AI) } (AII) }	2.49 (3)	(BI) (BII)	2.55 (3)
C(7) } C(11) }	2.81 (10)*	C(19) C(20)	2.68 (10)*
C(8) } C(10) }	2.83 (10)*	M(19,20)	2.58 (10)*
C(9)	2.85 (10)*	C(18) C(21)	2.97 (10)*
(AIII) } C''(7)† } C''(11)† }	2.55 (10)* 3.14 (10)* 3.06 (10)*	C''(22)†	2.68 (10)*
M''(7,11)	3.06 (10)*		
(AI)—Sm(A)—(AII)	123.5°	(BI)—Sm(B)—(BII)	120.5°
(AI)—Sm(A)—(AIII)	114.2	(BI)—Sm(B)—C''(22)†	109.4
(AI)—Sm(A)—M''(7,11)†	101.9	(BI)—Sm(B)—M(19,20)	117.3
(AIII)—Sm(A)—M''(7,11)†	93.9	Sm(B)—M(19,20)—(BIII)	81.8
Sm(A)—(AI)—C(3)	87.8	Sm(B)—(BI)—C(14)	91.5
Sm(A)—(AIII)—C(9)	91.0	Sm(B)—C''(22)—(BIII)''†	107.5
		M(19,20)—Sm(B)—C''(22)†	70.5

* E.s.d. value assigned.

† Those with double primes belong to the fourth ring, bonded to the metal atom as described in the text.

Fig.2. The electron density in the planes of the cyclopentadienyl rings. Contours are drawn at an interval of $1.5 \text{ e.}\text{\AA}^{-3}$.

found as in the previous synthesis, and no sensible interpretation of *A*III and *B*III was possible. Nevertheless, in this map, *A*I–*A*II as well as *B*I–*B*II were shown to be related by a mirror plane, and the two pairs (*A*I–*A*II and *B*I–*B*II) differed slightly in their inclination angles with respect to (010), as well as in their distances from their respective metal atoms. The positions of the carbon atoms of *A*I, *A*II, *B*I and *B*II were deduced from the difference map based on the assumption that the rings are rigid pentagons with edge lengths of 1.41–1.42 Å. A structure factor calculation including the four rings ($B=10.0$) reduced the agreement index to 14%. However, the agreement for a few low order reflexions, notably 022, 102, 062 and 222, was still very poor, and could only be improved if *A*III and *B*III were to have considerably different positions with respect to the metal atoms. At this stage, in order to reduce the anomalous peaks mentioned above, a correction for extinction was made. After a

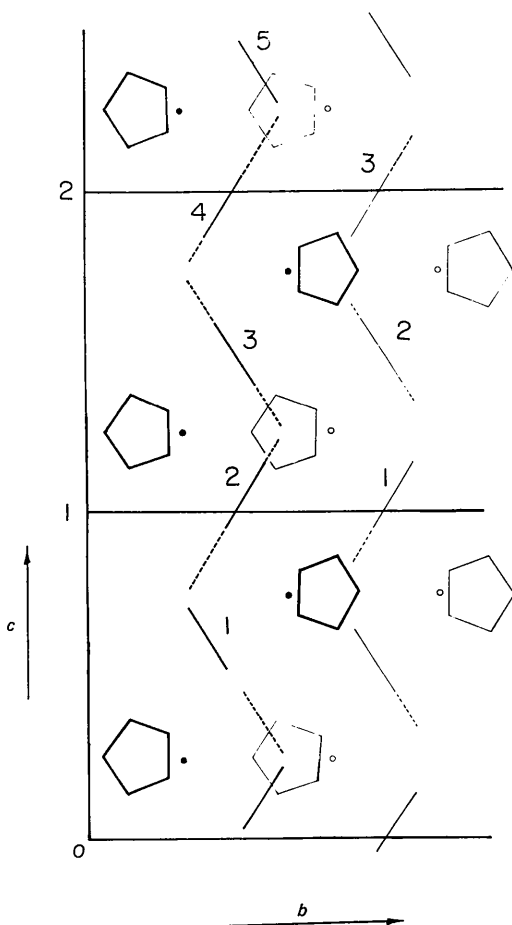


Fig. 3. Illustration of steps involved for the transition of *A*III and *B*III from one position to their respective mirror images, (100) projection. Dashed lines indicate the alternate positions for *A*III and *B*III that appeared on the difference map; solid lines are the positions *A*III and *B*III are assumed to have taken during the transition; solid circles for *Sm*(*A*), open circles for *Sm*(*B*).

rough estimation of the extinction coefficient from a plot of I_c/I_o against I_c , this extinction coefficient was included as a variable for least-squares calculations. This correction improved R to 13%. Another F_o-F_{Sm} synthesis was then computed and the situation was greatly improved: not only could *A*III and *B*III (identification see Fig. 1) be interpreted from the map (see Fig. 2), but also the other rings were much sharper and better defined. Background fluctuations were about $1.5 \text{ e.}\text{\AA}^{-3}$, except at the sites of the *Sm* atoms, where holes of about six electrons still remained. A full-matrix least-squares refinement was made on the following parameters: positional and anisotropic thermal parameters of *Sm*(*A*) and *Sm*(*B*); positional and anisotropic thermal parameters of *A*I, *A*II, *B*I and *B*II (with the restrictions that each is a rigid pentagon with edge length 1.41–1.42 Å and that *A*I–*A*II and *B*I–*B*II are mirror pairs, and also that their inclination angles with respect to (010) were fixed); positional and thermal parameters of *A*III and *B*III were not varied; isotropic temperature factors assigned for *A*III and *B*III were $B=10.0$. Refinement was stopped after three cycles of such calculations which reduced R to 12.5%. In the final cycle all the shifts were less than half their respective standard deviations, and the agreement for the above mentioned lower order reflexions was also satisfactorily improved. The resulting parameters are listed in Table 1, and the final set of structure factors in Table 2. The resulting positions of the carbon atoms are superposed on the final difference Fourier synthesis as shown in Fig. 2.

All the calculations were made on an IBM 1620 with programs written in this laboratory. Form factors used for *Sm* and *C* were those listed in *International Tables for X-ray Crystallography* (1962).

Results and discussion

All relevant distances and angles are listed in Table 3. In our interpretation of the difference Fourier syntheses (Fig. 2) *A*I, *A*II, *B*I and *B*II are definite, but *A*III and *B*III are not so definite because peaks representing a single carbon atom in *A*III and *B*III are only $3 \text{ e.}\text{\AA}^{-3}$ or less, which is only slightly higher than the background fluctuation. Nevertheless, we feel that this seems to be the most sensible interpretation we could suggest.

The quoted estimated standard deviations for carbon atoms (see Table 1) are indeed small for this type of structure containing heavy atoms. This is reasonable in view of the number of intrinsic conditions which have been incorporated into the least-squares calculations. In this way, a more detailed discussion of this structure becomes possible. The standard deviations for the inclination angles of rings were estimated directly from the final difference map.

A view along the [120] direction of the structure without disorder is shown in Fig. 1. In the *A* structure the *Sm* atom has three rings at nearly equal distances

[(2.49 ± 0.03 Å for (AI)–Sm(A) and (AII)–Sm(A), and 2.55 ± 0.10 Å for (AIII)–Sm(A)] π -bonded to it as in other sandwich compounds. AI and AII are mirror pairs, and $\angle(\text{AI})\text{--Sm(A)}\text{--}(\text{AII})$ is $123.5 \pm 4^\circ$. Ring AIII has been rotated downwards (or upwards), with the Sm atom as the pivot point, by about 30.8° from the (AI)–Sm(A)–(AII) plane (also the mirror plane). In this way, there will be room for Sm(A) to be bonded to a fourth ring AIII'', which is itself ring AIII for the Sm(A) atom a half period away and related to the original Sm(A) by a *c* glide plane normal to **b**. The fourth bond [Sm(A)–M''(7,11)] is a long π -bond (3.06 ± 0.10 Å). In this way all the type *A* Sm(C₅H₅)₃ molecules are joined to one another to form infinite zigzag chains along the *c* direction, the long cross-section of the chain lying nearly on $x=0$.

As for the *B* structure, the Sm atom has only two rings (BI and BII) sandwich-bonded to the metal in

the same way as in *A*, although their ring to Sm distances (2.55 ± 0.03 Å) and $\angle(\text{BI})\text{--Sm(B)}\text{--}(\text{BII})$ ($120.5 \pm 4^\circ$) are not significantly (2 e.s.d.'s for distances, 1 e.s.d. for the angle) different from the *A* structure values.

The most remarkable differences between these two types of structures are the positions of AIII and BIII on one hand and the temperature factors of Sm(A) and Sm(B) on the other. BIII, which has nearly the same inclination angle with respect to (001) as AIII, is as much as 0.6 Å further away along the plane of the ring from the AIII position (see Fig. 1 and Fig. 3). In this way, all the *B* type Sm(C₅H₅)₃ molecules are joined up to form similar infinite chains as in the *A* type. The second remarkable difference between the *A* and *B* structures is the observed temperature factor, that for Sm(B) being about four times greater than that for Sm(A). The best explanation that we can offer is that Sm(B) is disordered and therefore has several

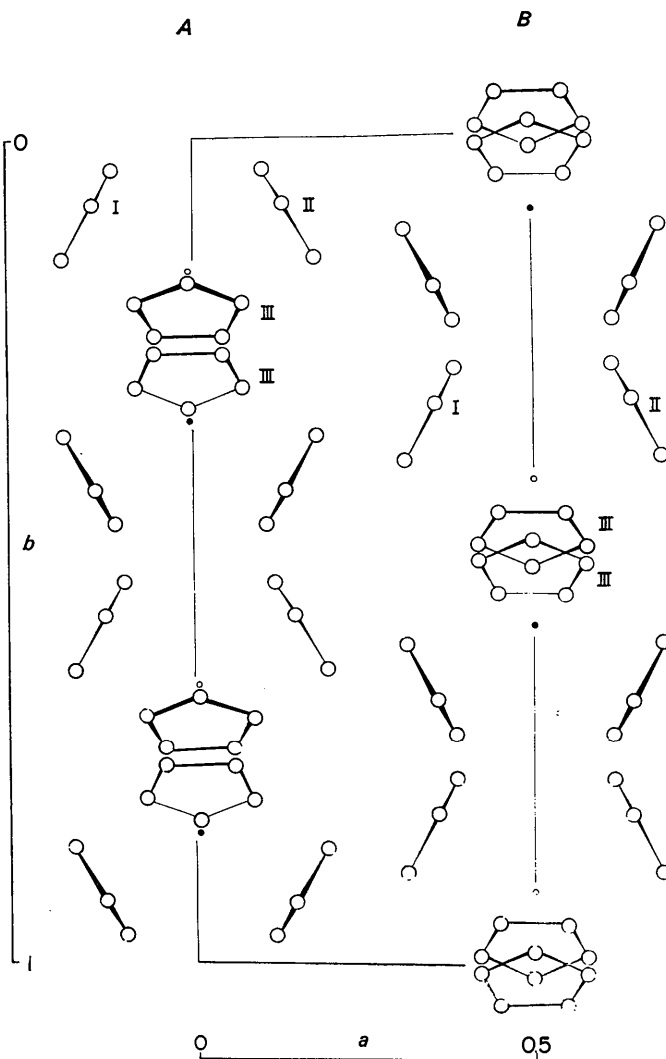


Fig. 4. Projection along *c*. All, III and III' have one half the weight. Large open circles represent carbon atoms, small solid circles are Sm on $\frac{1}{4}$, small open circles are Sm on $\frac{3}{4}$.

positions in the near vicinity of the mean position which it could occupy. This proposition conforms to some extent with the trend of $\text{Sm}(A)-(AI)$ [or (AII)] to be slightly shorter than $\text{Sm}(B)-(BI)$ [or (BII)] and the angle $(AI)-\text{Sm}(A)-(AII)$ to be a little greater than the angle $(BI)-\text{Sm}(B)-(BII)$.^{*} This situation is to some degree similar to our result on the crystal structure of $\text{Be}(\text{C}_5\text{H}_5)_2$ at -100°C (Wong, Chao, Chieh & Lee, 1969) in which the Be is found to be able to occupy two alternative positions [not on the fivefold rotation axis, as suggested by the electron diffraction results (Almenningen, Bastiansen & Haaland, 1964)].

A rough estimation on the basis of Pauling's single bond radii for Sm (1.15 Å) and for carbon (0.77 Å) (Pauling, 1960) and a Schomaker & Stevenson (1941) correction indicates that approximately three pairs of electrons are responsible for bonding between the metal atoms and cyclopentadienyl rings in both *A* and *B*. There is about 37% partial ionic character in the Sm-C bond, which suggests that the interaction between samarium and carbon is more covalent in character. This seems also to be closely related with the fact that the rings in this structure have a definite preferred orientation.

As for the disorder in the positions of *AIII* and *BIII*, it could be either static disorder, *i.e.* that there is equal probability that the crystal will grow along the *c* or along the $-\text{c}$ direction, or dynamic disorder, *i.e.* that both *AIII* and *BIII* will not have to cross a very high potential barrier to obtain their respective mirror images. In Fig. 3, the junction structure (for static disorder) or the transition mechanism (for dynamic disorder) for *AIII* and *BIII* is illustrated in steps. In

^{*} Neither $\text{Sm}(A)$ nor $\text{Sm}(B)$ is on the fivefold axes of *AI* (or *AII*), and *BI* (or *BII*) respectively. However, the deviations from the axes of $\text{Sm}(B)$, (2 to 3 e.s.d.'s) are greater than that of $\text{Sm}(A)$ (~ 1 e.s.d.). This feature is also consistent with the disorder of $\text{Sm}(B)$.

the scheme proposed, a rough calculation shows that only small strains are involved in each step.

The temperature factor for $\text{Sm}(A)$ is about 1.6 along *b* and *c*, and about 1.1 along *a*. Temperature factors for *AI*, *AII*, *BI* and *BII* are of the same order within their respective estimated standard deviations. The component along the plane of the ring but normal to *c* ($B=18$) is about twice as large as that normal to the plane of the ring ($B=9$), whereas the component parallel to *c* is between the above two values ($B=12$).

A projection of the structure along *c* is shown in Fig. 4 showing the close packing of the cross sections of the chains, and illustrating the slight difference between the two subcells mentioned above. All the inter-chain distances are normal van der Waals distances, from 3.55 Å upwards.

The authors are grateful to Dr Li-chen Wang for assistance in preparing this compound, and to Mr Chueng-tan Chen for measuring the density.

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