Journal of Organometallic Chemistry, 69 (1974) 225—233

THE MOLECULAR AND CRYSTAL STRUCTURE OF TETRACYCLOPENTADIENYLURANIUM(IV)

JOHN H. BURNS

Transuranium Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37830 (U.S.A.)

(Received August 24th, 1973)

Summary

The crystal structure of $(C_5H_5)_4U$ was determined from single-crystal X-ray diffraction data. The body-centered tetragonal unit cell contains two molecules and has dimensions *a* 8.635(2) and *c* 10.542(3) Å. A structural model based on a random mixture of a pair of enantiomorphic molecules in the crystal accounts for the space-group symmetry, $I\bar{4}2m$, while individual molecules have point symmetry S_4. In each molecule, planar C_5 rings are in a regular tetrahedral array around a uranium atom and are *pentahapto*-bonded to it. The C—C bond lengths are all equal within experimental error and have a mean value of 1.386(5) Å; the same is true for the U—C bonds whose mean is 2.807(11) Å.

Introduction

Research has greatly increased on organometallic compounds of the tetravalent actinides since the synthesis of uranocene (dicyclooctatetraenyluranium(IV)) was reported [1] in 1968 and it was shown [2] to be a π sandwich complex. In addition to the analogous metallocenes with Th [3], Np [4], and Pu [4], several similar compounds have been prepared [5—7] in which the cyclooctatetraenyl dianion has various alkyl substituents and the metals are Th, U, Np, and Pu. Other work on U^{IV} organometallic compounds has included synthesis of σ-bonded aryl and alkyl complexes [8, 9] and structural studies [10—12] of several substituted cyclopentadienyl derivatives of U^{IV}.

Tetracyclopentadienyluranium(IV), which was synthesized [13] more than eleven years ago, and its analogues containing Th [14], Pa[15], and Np [16] have been the subject of numerous investigations; but the conclusion reached have been limited by lack of knowledge of the molecular structure. These studies have included proton NMR [17] on $(C_5H_5)_4U$, magnetic susceptibility of $(C_5H_5)_4U$ [18]

and $(C_5H_5)_4Np$ [19], Mössbauer absorption [18] by $(C_5H_5)_4Np$, infrared absorption [20, 21] of $(C_5H_5)_4Th$, $(C_5H_5)_4Pa$, $(C_5H_5)_4U$, and $(C_5H_5)_4Np$, and theoretical treatment [22] of the crystal-field splittings in $(C_5H_5)_4U$. Although the early proposal [13] that $(C_5H_5)_4U$ forms a tetrahedral molecule was plausible, some uncertainty was introduced when the structures became known for $(C_5H_5)_4Zr$ [23], $(C_5H_5)_4Ti$ [24], and $(C_5H_5)_4Hf$ [25], none of which have four *pentahapto*-bonded rings. Consequently an X-ray diffraction analysis of the structure of $(C_5H_5)_4U$ was performed; a preliminary account has been given [26], and the details are to be presented here.

Experimental

Tetracyclopentadienyluranium(IV) was prepared by reaction of UCl_4 and KC_5H_5 in benzene, using the original method [13]. The product was extracted with benzene to produce large, deep red, multifaceted crystals*. A single-crystal specimen was selected which had a rhombohedral shape and a maximum dimension of about 0.024 cm. Because of its sensitivity to air the crystal was sealed in a thin-walled glass tube with an Ar atmosphere.

Precession X-ray photographs showed the crystal symmetry to be tetragonal. Reflections are absent when $h + k + l$ is odd, indicating that the lattice is body centered. Subsequent careful examination by a diffractometer confirmed that this is the pattern of absences, and measurement of 2θ values of 9 reflections in the range 41 - 47° were used to give the best values of the unit-cell dimensions by least-squares refinement. They are a 8.635(2) and c 10.542(3) Å (T 25°C, $\lambda(\text{Mo-K}_{\alpha_1}) = 0.70926$ Å). The calculated crystal density is 2.10 $g{\cdot}cm^{-3}$ for $Z = 2$.

Measurement of intensities was carried out with a computer-controlled Picker X-ray diffractometer employing Mo-K_α (Nb filtered) radiation at a 2° take-off angle. The 1194 reflections found in one octant of reciprocal space out to $2\theta = 78°$ were recorded by θ—2θ scanning. Scan ranges varied from 0.8° at the lowest 2θ to 1.3° at the highest; the backgrounds were counted at each end of the scans and averaged. A reference reflection measured hourly varied in intensity no more than 1.3% from the average throughout the data collection period.

Structure determination and refinement

In order to correct the intensities for absorption, the six planes bounding the crystal were measured with a microscope and transmission factors were calculated** by the method of Busing and Levy [27]. These ranged from 0.16 to

---

[*] Crystals were supplied for this work by Dr.P. Laubereau of the Technical University of Munich and by Dr.B. Kanellakopulos of the Nuclear Research Center in Karlsruhe, Germany.

[**] The following computer programs, written at ORNL for the IBM 360, were used in this work: DATALIB, a data reduction program by Ellison and Levy incorporating ORABS, the absorption program of Wehe, Busing, and Levy; FORDAPER, a modification of Zalkin's Fourier program; ORXFLS, a version of the Busing-Levy least squares; ORFFE, a function and error program by Busing, Martin, and Levy; ORTEP by Johnson for plotting; BSPLAN for obtaining the best plane through atoms and EDIT for listing structure factors, both by Brown.

0.26 and were based on a linear absorption coefficient of 126 cm^{-1} for the compound. By application of these corrections, the Lorentz and polarization factors, and by interpolation between reference reflections, the data were converted to a set of relative squared structure factors, F_o^2.

There were no systematic absences other than those due to the body-centered lattice. Hence, until the Laue symmetry could be determined, eight space groups had to be considered as possibilities. From the observed monotonic decline in intensity with increasing Bragg angle, it was deduced that the U atoms lie at the origin and body center and dominate the scattering. Thus, although the intensities appeared to have $4/mmm$ symmetry, i.e., intensities of reflections (hkl) and (khl) differed by only one or two standard errors, the lower symmetry $4/m$ was initially assumed. With this symmetry and the appropriate data set a Patterson map was calculated. It contained 80 peaks at distances from the origin corresponding to U—C vectors and had essentially $4/mmm$ symmetry. Forty of these maxima were easily assigned to four cyclopentadienyl rings of one $(C_5H_5)_4U$ molecule and to a centrosymmetric set generated by Patterson symmetry. The other forty peaks were attributable to another set of rings which were the mirror image of the original by reflection in a plane along (110). Because of stoichiometric and physical limitations, both sets of C atoms cannot exist simultaneously; hence a disordered structure seemed required to explain the Patterson map.

Nevertheless an attempt was made to refine the structure with an ordered model using only one set of 20 C atoms in the asymmetric unit. Least-squares refinement of this model (space group $I\bar{4}$) converged to yield an agreement index, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, of 0.0261 and a standard deviation of an observation of unit weight, σ_1, of 1.259. (In order to emphasize the relatively small contribution of the C atoms to the intensities, it is noted that for a model with U atoms alone, $R = 0.052$.) Yet, a subsequent electron density map still showed the presence of both mirror-related molecules each with C atoms containing half the normal number of electrons. Thus the disordered model was chosen and refined in space group $I\bar{4}2m$ with 700 observations to $R = 0.0207$ and $\sigma_1 = 1.003$, a highly significant improvement. A refinement of occupancy factors yielded fractions of the two forms which are equal within one standard deviation; exact equality was assumed in subsequent calculations. In the last stage of refinement structure-factor calculations included H atoms at 1 Å radial distances from the planar C_5 rings, with isotropic thermal parameters of 5 Å^2. A final difference Fourier map showed no excursions greater than ± 0.5 $e/\text{Å}^3$ except for some residual peaks at 1.6 $e/\text{Å}^3$ around the U atom position.

The least-squares refinement involved minimization of $\Sigma[1/\sigma^2(F_o^2)][F^2-F_o^2]^2$ in which F is the calculated structure factor, scaled and corrected for isotropic extinction [28] and $\sigma^2(F_o^2) = \sigma_c^2 + (0.03\,F_o^2)^2$, σ_c^2 being the variance due to counting statistics. Atomic scattering factors for U, C, and H were those of Cromer and Waber [29] and the U atom was corrected for anomalous dispersion [30]. Because the imaginary component of anomalous dispersion is large, it was possible to determine the absolute configuration of the crystal by comparing the R index (0.0207) from refined parameters describing the structure with that (0.0263) from the refined structure after inversion through the origin [31]. Hamilton's [32] test indicates this difference to be significant at greater

TABLE 1

POSITIONAL AND THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS[a]

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
U	0	0	0	65.4(3)	65.4	48.4(2)	0	0	0
C(1)	0.261(3)	0.180(3)	−0.049(2)	161(32)	250(39)	110(10)	−110(30)	31(13)	−23(14)
C(2)	0.138(3)	0.273(2)	−0.091(2)	229(42)	100(17)	243(45)	15(27)	117(34)	75(31)
C(3)	0.062(2)	0.208(4)	−0.194(2)	183(21)	346(63)	162(26)	126(33)	76(23)	180(34)
C(4)	0.160(2)	0.087(2)	−0.223(2)	197(30)	208(39)	84(9)	−57(32)	32(12)	35(13)
C(5)	0.276(2)	0.062(2)	−0.135(1)	117(14)	173(19)	102(11)	0(15)	48(10)	17(13)
H(1)	0.325	0.199	0.028	$B = 5\text{Å}^2$					
H(2)	0.109	0.374	−0.051						
H(3)	−0.037	0.243	−0.235						
H(4)	0.148	0.022	−0.301						
H(5)	0.355	−0.023	−0.133						

[a] The U atom is in 2(*a*), and the other atoms are in 16(*j*) with half occupancy [40]. Thermal parameters are for the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Numbers in parentheses are the standard deviations in the last significant digits.

TABLE 2

STRUCTURE FACTORS ON AN ABSOLUTE SCALE

L	OBS	CAL
**	0 0	L **
2	125	125
4	128	128
6	94	94
8	78	78
10	57	57
12	37	37
14	33	33
16	20	20
18	12	14
**	0 1	L **
1	201	190
3	106	106
5	124	126
7	81	82
9	74	75
11	46	46
13	38	38
15	25	25
17	16	17
**	0 2	L **
0	90	91
2	106	107
4	122	124
6	101	102
8	82	83
10	61	61
12	44	44
14	29	30
16	20	26
18	13	13
**	0 3	L **
1	129	127
3	114	116
5	92	93
7	94	95
9	81	82
11	49	49
13	33	33
15	25	24
17	15	16
**	0 4	L **
0	127	129
2	121	123
4	89	91
6	89	90
8	64	65
10	49	48
12	36	37
14	25	25
16	18	19
18	12	11
**	0 5	L **
1	95	93
3	102	103
5	91	90
7	84	84
9	51	51
11	43	42
13	29	29
15	19	21
17	14	13
**	0 6	L **
0	77	79
2	88	89
4	86	88
6	63	63
8	54	53
10	44	44
12	30	31
14	23	22
16	11	15
**	0 7	L **
1	81	82
3	74	75
5	56	56
7	52	53
9	43	43
11	31	30
13	24	24
15	18	16
**	0 8	L **
0	64	63
2	67	67
4	54	55
6	49	49
8	44	42
10	32	31
12	27	28
14	18	17
**	0 9	L **
1	47	47
3	53	54
5	46	47
7	39	39
9	30	30
11	27	27
13	18	17
15	14	12
**	0 10	L **
0	43	42
2	45	45
4	40	41
6	34	35
8	29	29
10	25	24
12	14	17
14	14	13
**	0 11	L **
1	39	40
3	33	34
5	29	30
7	27	27
9	21	22
11	16	16
13	14	13
**	0 12	L **
0	30	30
2	29	29
4	29	27
6	24	24
8	20	20
10	15	15
**	0 13	L **
1	22	22
3	24	23
5	20	21
7	16	17
9	13	14
**	0 14	L **
0	19	20
2	19	19
4	16	17
6	15	15
**	0 15	L **
1	18	15
3	12	13
**	1 1	L **
0	163	164
2	143	140
4	144	145
6	100	100
8	77	78
10	61	61
12	43	42
14	32	31
16	20	20
18	10	14
**	1 2	L **
1	133	128
3	148	148
5	110	111
7	83	85
9	66	66
11	51	51
13	36	35
15	23	24
17	17	16
**	1 3	L **
0	129	130
2	148	147
4	96	98
6	92	91
8	72	72
10	54	53
12	40	43
14	28	27
16	20	20
18	12	12
**	1 4	L **
1	134	133
3	102	102
5	85	86
7	78	78
9	55	55
11	45	45
13	30	30
15	22	23
17	11	14
**	1 5	L **
0	97	97
2	98	97
4	91	92
6	77	77
8	59	57
10	49	49
12	34	34
14	24	24
16	16	16
**	1 6	L **
1	85	83
3	82	84
5	74	74
7	59	58
9	52	50
11	36	36
13	26	25
15	18	19
17	13	12
**	1 7	L **
0	82	82
2	76	75
4	63	64
6	56	58
8	53	51
10	36	35
12	25	27
14	19	23
16	12	13
**	1 8	L **
1	68	66
3	61	61
5	52	52
7	48	48
9	35	35
11	29	28
13	19	21
15	14	14
**	1 9	L **
0	50	49
2	53	53
4	48	50
6	43	43
8	33	33
10	28	28
12	22	21
14	15	14
**	1 10	L **
1	45	44
3	41	42
5	36	37
7	31	31
9	25	26
11	20	20
13	14	14
**	1 11	L **
0	40	40
2	38	36
4	31	32
6	28	28
8	24	25
10	17	19
12	14	14
**	1 12	L **
1	28	29
3	28	28
5	26	25
7	22	22
9	17	18
11	13	14
**	1 13	L **
0	24	22
2	22	23
4	22	22
6	19	19
8	15	16
**	1 14	L **
1	19	19
3	19	17
5	17	16
7	15	14
**	1 15	L **
0	16	15
2	15	14
**	2 2	L **
0	111	113
2	167	169
4	121	123
6	87	87
8	65	66
10	94	94
12	41	41
14	27	28
16	19	19
18	13	13
**	2 3	L **
1	137	137
3	120	122
5	87	87
7	78	79
9	56	57
11	48	46
13	31	32
15	23	23
17	14	15
**	2 4	L **
0	116	119
2	105	107
4	88	88
6	65	64
8	66	65
10	51	51
12	36	38
14	26	28
16	18	17
**	2 5	L **
1	100	100
3	85	86
5	85	84
7	94	94
9	54	54
11	39	40
13	27	28
15	19	19
17	12	13
**	2 6	L **
0	92	92
2	75	76
4	75	78
6	65	64
8	53	52
10	42	41
12	29	29
14	22	22
16	12	15
**	2 7	L **
1	75	74
3	61	62
5	61	61
7	53	53
9	42	42
11	30	29
13	24	23
15	15	16
**	2 8	L **
0	67	65
2	60	60
4	54	55
6	50	51
8	40	40
10	29	30
12	24	24
14	17	17
**	2 9	L **
1	56	54
3	50	50
5	44	45
7	35	36
9	28	29
11	23	24
13	14	17
**	2 10	L **
0	48	46
2	42	42
4	37	38
6	32	33
8	26	28
10	22	23
12	17	16
**	2 11	L **
1	36	36
3	32	32
5	29	30
7	28	26
9	20	22
11	16	16
**	2 12	L **
0	29	28
2	27	28
4	27	27
6	22	23
8	19	19
10	15	15
**	2 13	L **
1	21	23
3	22	22
5	19	19
7	18	17
9	13	14
**	2 14	L **
0	17	18
2	17	18
4	16	16
6	15	15
**	2 15	L **
1	14	14
**	3 3	L **
0	99	100
2	105	107
4	93	94
6	87	88
8	67	68
10	51	50
12	37	36
14	26	27
16	19	18
**	3 4	L **
1	92	91
3	93	91
5	91	91
7	71	71
9	56	56
11	40	40
13	31	30
15	22	20
17	14	13
**	3 5	L **
0	102	102
2	87	88
4	88	88
6	88	86
8	54	53
10	43	43
12	31	31
14	24	23
16	14	15
**	3 6	L **
1	88	86
3	75	76
5	68	68
7	51	50
9	44	44
11	33	32
13	25	25
15	16	17
**	3 7	L **
0	71	69
2	63	63
4	62	63
6	53	53
8	44	44
10	34	34
12	25	25
14	18	18
16	12	13
**	3 8	L **
1	59	57
3	55	55
5	50	51
7	41	41
9	35	34
11	27	28
13	20	19
15	13	13
**	3 9	L **
0	54	52
2	51	50
4	44	45
6	37	38
8	31	31
10	25	26
12	20	19
14	11	14
**	3 10	L **
1	41	41
3	39	38
5	33	35
7	30	30
9	24	24
11	18	19
13	13	14
**	3 11	L **
0	34	33
2	31	32
4	29	31
6	28	28
8	22	23
10	18	18
12	13	13
**	3 12	L **
1	27	28
3	27	27
5	23	24
7	20	20
9	15	15
11	13	13
**	3 13	L **
0	25	23
2	22	22
4	19	20
6	15	17
8	13	15
**	3 14	L **
1	18	17
3	16	16
5	15	15
**	3 15	L **
0	13	13
**	4 4	L **
0	86	87
2	85	85
4	93	92
6	69	70
8	57	57
10	43	43
12	31	32
14	24	24
16	15	15
**	4 5	L **
1	89	88
3	94	94
5	69	68
7	54	52
9	46	46
11	33	33
13	25	26
15	17	17
17	12	12
**	4 6	L **
0	78	78
2	74	75
4	66	67
6	54	53
8	47	45
10	35	35
12	26	27
14	19	19
16	11	13
**	4 7	L **
1	60	60
3	62	63
5	55	55
7	46	45
9	38	37
11	29	28
13	21	20
15	19	14
**	4 8	L **
0	53	51
2	55	55
4	49	50
6	42	41
8	36	36
10	29	29
12	21	21
14	16	15
**	4 9	L **
1	48	47
3	44	44
5	36	37
7	32	33
9	27	28
11	21	21
13	15	15
**	4 10	L **
0	40	38
2	37	37
4	34	35
6	31	31
8	25	26
10	21	20
12	16	15
**	4 11	L **
1	31	30
3	30	30
5	28	28
7	23	23
9	18	18
11	14	15
**	4 12	L **
0	27	25
2	25	26
4	23	23
6	19	20
8	15	17
10	13	14
**	4 13	L **
1	21	21
3	19	19
5	17	17
7	15	15
**	4 14	L **
0	14	16
2	16	16
4	14	15
**	5 5	L **
0	78	77
2	75	75
4	62	62
6	55	55
8	52	51
10	36	36
12	28	28
14	19	19
16	13	14
**	5 6	L **
1	68	65
3	60	60
5	54	53
7	55	54
9	39	38
11	30	30
13	20	21
15	16	15
**	5 7	L **
0	55	54
2	59	58
4	52	52
6	49	48
8	38	38
10	31	29
12	22	22
14	16	15
**	5 8	L **
1	52	51
3	49	49
5	40	41
7	36	36
9	28	29
11	23	22
13	17	16
**	5 9	L **
0	45	44
2	42	42
4	38	37
6	32	33
8	29	29
10	21	21
12	15	16
**	5 10	L **
1	36	35
3	33	33
5	29	30
7	25	27
9	18	21
11	17	16
**	5 11	L **
0	30	29
2	28	29
4	26	27
6	22	23
8	20	19
10	13	16
**	5 12	L **
1	26	24
3	22	23
5	17	20
7	13	17
9	15	15
**	5 13	L **
0	20	19
2	18	18
4	16	17
5	14	16
**	5 14	L **
1	14	15
3	14	14
**	6 6	L **
0	57	56
2	58	58
4	49	49
6	54	53
8	40	39
10	29	29
12	24	24
14	13	16
**	6 7	L **
1	56	54
3	50	50
5	45	45
7	36	37
9	29	26
11	26	24
13	16	16
**	6 8	L **
0	49	47
2	46	45
4	39	40
6	34	35
8	27	28
10	24	24
12	16	17
14	13	13
**	6 9	L **
1	39	38
3	35	35
5	32	32
7	28	29
9	23	24
11	20	17
13	13	13
**	6 10	L **
0	33	32
2	31	31
4	30	29
6	27	26
8	21	21
10	16	16
12	13	13
**	6 11	L **
1	27	27
3	25	26
5	21	22
7	18	19
9	14	16
**	6 12	L **
0	21	22
2	21	21
4	20	19
6	17	17
8	15	15
**	6 13	L **
1	16	17
3	13	15
5	14	15
**	6 14	L **
0	14	14
2	11	14
**	7 7	L **
0	49	49
2	48	47
4	42	42
6	36	35
8	26	25
10	26	25
12	19	18
14	11	13
**	7 8	L **
1	40	39
3	37	37
5	34	34
7	29	27
9	25	25
11	20	19
13	13	13
**	7 9	L **
0	33	33
2	31	31
4	32	31
6	26	28
8	24	24
10	20	18
12	16	13
**	7 10	L **
1	29	28
3	25	27
5	25	25
7	22	21
9	13	15
11	15	13
**	7 11	L **
0	23	24
2	25	24
4	22	22
6	16	18
8	15	15
**	7 12	L **
1	21	19
3	18	18
5	18	15
7	15	15
**	7 13	L **
0	17	15
2	15	15
4	15	14
**	8 8	L **
0	38	34
2	33	32
4	32	32
6	25	27
8	24	24
10	21	20
12	15	13
**	8 9	L **
1	29	29
3	28	28
5	25	25
7	22	22
9	20	18
11	14	13
**	8 10	L **
0	27	26
2	25	25
4	23	23
6	21	19
8	15	15
10	13	12
**	8 11	L **
1	19	21
3	19	20
5	19	18
7	13	15
**	8 12	L **
0	15	17
2	14	15
4	17	15
6	15	14
**	8 13	L **
1	14	14
**	9 9	L **
0	30	27
2	26	26
4	23	23
6	20	19
8	19	17
10	12	12
**	9 10	L **
1	22	22
3	20	21
5	17	18
7	17	16
**	9 11	L **
0	17	17
2	16	17
4	16	16
6	14	15
**	9 12	L **
1	15	15
3	12	14
**	10 10	L **
0	18	17
2	16	18
4	17	16
6	13	15
**	10 11	L **
1	15	15
3	14	14

than the 0.995 level. The parameters given in Table 1 represent the absolute configuration obtained in this way. The observed and calculated structure factors on an absolute scale are listed in Table 2.

Description and discussion of the structure

In each molecule of $(C_5H_5)_4U$ the U atom is surrounded by h^5 (*pentahapto*)-bonded C_5H_5 rings in a tetrahedral array as shown in Fig. 1. The S_4 symmetry of the molecule requires its four rings to be equivalent; and the angle from the centroid of one ring to the U atom to the centroid of another ring is tetrahedral within ± 0.6°, although not required to be by symmetry. These molecules are packed in the crystal with a body-centered tetragonal unit cell as shown in Fig. 2. There is disorder, however, and each molecular site contains either the molecule pictured in Fig. 1 or its enantiomorph, producing an average structure containing about equal quantities of each. This disorder probably results from the fact that the two forms of the molecule are of equal energy and that their nearly

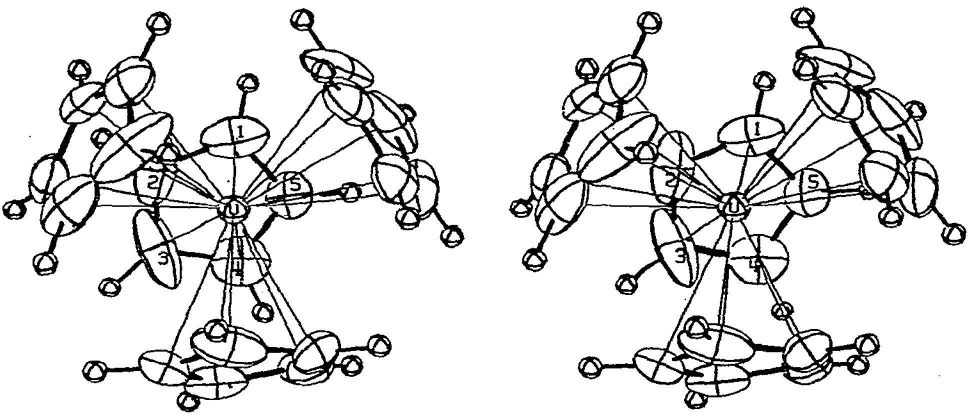

Fig. 1. Stereoscopic view of one molecule of $(C_5H_5)_4U$ with non hydrogen atoms represented by 50% probability thermal ellipsoids.

spherical exterior allows either to fit about equally well in a given site. From consideration of intermolecular contacts which would occur between symmetry-related molecules of the same handedness (ordered model) and between those of opposite handedness (disordered), it is seen that there are about the same number in each case; thus no large domains of order are expected to exist. This is a tentative conclusion because of the fact that the contacts considered all involve H atoms, whose positions have not actually been determined.

Bond lengths and angles are listed in Table 3. The C—C bonds are all equal within experimental error, the greatest difference between any pair being 0.017 Å between C(1)—C(2) and (C3)—C(4) with a standard deviation of 0.048 as es-

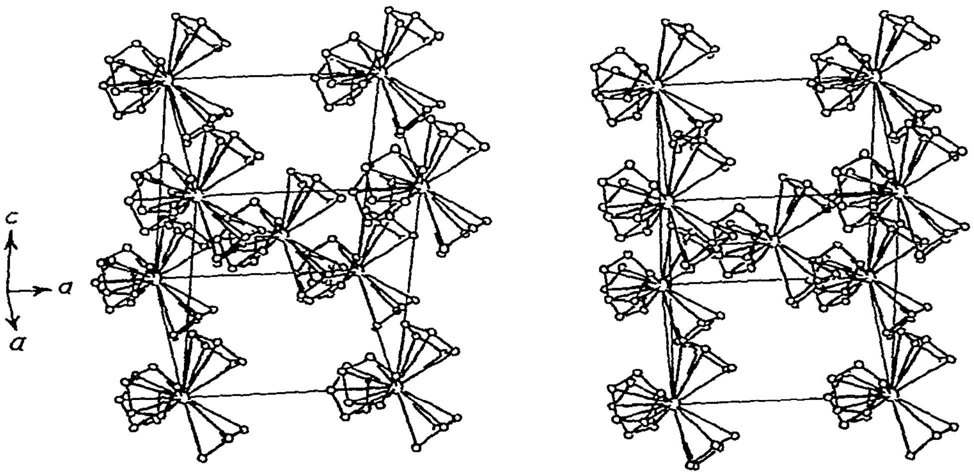

Fig. 2. Stereoscopic view of one unit cell of $(C_5H_5)_4U$.

TABLE 3

BOND DISTANCES (Å) AND ANGLES (°)

C(1)—C(2)	1.396(30)		U—C(1)	2.785(22)
C(2)—C(3)	1.393(38)		U—C(2)	2.813(18)
C(3)—C(4)	1.380(33)		U—C(3)	2.777(16)
C(4)—C(5)	1.391(24)		U—C(4)	2.833(17)
C(5)—C(1)	1.371(23)		U—C(5)	2.829(14)
C(1)—C(2)—C(3)		112.2(19)		
C(2)—C(3)—C(4)		100.7(18)		
C(3)—C(4)—C(5)		114.5(23)		
C(4)—C(5)—C(1)		104.7(20)		
C(5)—C(1)—C(2)		107.1(23)		

timated from the variance-covariance matrix. Pairs of U—C distances do not differ significantly either, the extreme being 0.055 Å with a standard deviation of 0.029 Å. The mean values of C—C and U—C distances are 1.386(5) Å and 2.807 (11) Å, respectively, with each standard error of the mean in parentheses. The range of interior angles for the pentagon is found to be rather large, the extremes differing by 3.7 σ's, but there is no apparent chemical reason why the distortion should be regarded as real; and in other respects the ring is a typical aromatic cyclopentadienyl system. The five C atoms are within about 0.05 Å of the least-squares-determined best plane, whose equation, in fractional crystal coordinates, is $5.17x + 4.89y + 5.96z = 2.55$. Individual deviations, in Å, are C(1), —0.024; C(2), 0.047; C(3), —0.052; C(4), 0.039; C(5), —0.010. The perpendicular distance from the plane to the U atom is 2.55 Å.

Thermal motions of the atoms are represented in Fig. 1 by 50% probability ellipsoids, except for the H atoms which are shown as arbitrarily small spheres. The motion of the U atom is almost isotropic, but the C-atom ellipsoids are generally elongated in directions approximately tangential to the rings, indicating some oscillation of the rings about their 5-fold axes. The rms amplitudes of vibration along the major axes of the ellipsoids range from 0.28 to 0.47 Å. A more detailed treatment of the thermal motion does not seem justified in view of the limitation on accuracy of the data caused by absorption and of the disordered light atoms in the structure.

The determination that $(C_5H_5)_4U$ is a tetrahedral molecule has verified the configuration that was assumed in the interpretation of numerous physico-chemical measurements mentioned in the Introduction and provides quantitative data for further calculations in some instances, e.g., crystal-field splittings [22]. Also, the structures of $(C_5H_5)_4Th$, $(C_5H_5)_4Pa$, and $(C_5H_5)_4Np$ are now known since isomorphism was already indicated by X-ray powder diffraction [18, 20] and by infrared data [20, 21].

Recently, there have been several precise structure determinations of organometallic U^{IV} π complexes. These have involved cyclopentadienyl [12], benzylcyclopentadienyl [11], indenyl [10], cyclooctatetraenyl [2], and tetramethylcyclooctatetraenyl [33] ligands. The last two each form true sandwich π complexes; and experimental [1, 4, 5] and theoretical [1, 34] work has been reported suggesting that in these the bonding is covalent and involves 5*f* orbitals of uranium. Those compounds containing cyclopentadienyl rings also are of the "sandwich" type provided the name can include tetrahedral arrays of planar

TABLE 4

U^{IV}—C BOND LENGTHS IN VARIOUS COMPOUNDS

Compound	Mean π-bond length (Å)	Reference
$(C_8H_8)_2U$	2.65	2
$[(CH_3)_4C_8H_4]_2U$	2.66	33
$(C_5H_5)_3UC{\equiv}CC_6H_5$	2.68	12
$(C_6H_5CH_2C_5H_4)_3UCl$	2.73	11
$(C_5H_5)_3UCl$	2.74[a]	36
$(C_9H_7)_3UCl$	2.79	10
$(C_5H_5)_4U$	2.81	This work

[a] Not of comparable accuracy to the others listed.

rings. There is scattered chemical [13, 35] and physical evidence [17, 18] for some covalency in these compounds too, the most direct in the case of $(C_5H_5)_4U$ being the Mössbauer studies of isomorphous $(C_5H_5)_4Np$ [18].

In all these structures of U^{IV} complexes with C_5 and C_8 rings there exists essentially equal attachment of the metal to all the C atoms of each ring, i.e., h^5 and h^8 bonds, although the U—C bond lengths vary over a considerable range as shown in Table 4. Leong et al. [11] have proposed a linear relationship between the bond length and the charge on the ligand; but this does not account for all the values in this list where, for some of the compounds, steric factors must also be important. In any case the fact that, in spite of variation in bond lengths (and coordination number), the bonding remains *polyhapto* throughout these examples is possibly indicative of covalent character in these tetravalent uranium compounds. Such is not the observation for cyclopentadienides of *trivalent* lanthanides (and actinides) in which there are examples of mixtures of h^5 and h^1 bonding in $(C_5H_5)_3Sm$ [37] and $(CH_3C_5H_4)_3Nd$ [38]. This may be attributed to the greater ionic character [39] of the bonds in these compounds whereby the structure achieved depends on packing of ions more so than in those formed involving directional covalent bonding.

Acknowledgements

This research was sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

References

1 A. Streitwieser and U. Müller-Westerhoff, J. Amer. Chem. Soc., 90 (1968) 7364.
2 A. Zalkin and K.N. Raymond, J. Amer. Chem. Soc., 91 (1969) 5667.
3 A. Streitwieser and N. Yoshida, J. Amer. Chem. Soc., 91 (1969) 7528.
4 D.G. Karraker, J.A. Stone, E.R. Jones and N. Edelstein, J. Amer. Chem. Soc., 92 (1970) 4841.
5 A. Streitwieser, D. Dempf, G.N. LaMar, D.G. Karraker and N. Edelstein, J. Amer. Chem. Soc., 93 (1971) 7343.
6 A. Streitwieser and C.A. Harmon, Inorg. Chem., 12 (1973) 1102.
7 D.G. Karraker, Inorg. Chem., 12 (1973) 1105.
8 A.E. Gebala and M. Tsutsui, Chem. Lett. (1972) 775; J. Amer. Chem. Soc., 95 (1973) 91.
9 T.J. Marks and A.M. Seyam, J. Amer. Chem. Soc., 94 (1972) 6545.
10 J.H. Burns and P.G. Laubereau, Inorg. Chem., 10 (1971) 2789.
11 J. Leong, K.O. Hodgson and K.N. Raymond, Inorg. Chem., 12 (1972) 1329.
12 J.L. Atwood, C.F. Hains, M. Tsutsui and A.E. Gebala, J. Chem. Soc., Chem. Commun., (1973) 452.
13 E.O. Fischer and Y. Hristidu, Z. Naturforsch. B, 17 (1962) 275.
14 E.O. Fischer and A. Treiber, Z. Naturforsch. B, 17 (1962) 276.

15 F. Baumgärtner, E.O. Fischer, B. Kanellakopulos and P. Laubereau, Angew. Chem., 81 (1969) 182; Angew. Chem. Int. Ed. Engl., 8 (1969) 202.

16 F. Baumgärtner, E.O. Fischer, B. Kanellakopulos and P. Laubereau, Angew. Chem., 80 (1968) 661; Angew. Chem. Int. Ed. Engl., 7 (1968) 634.

17 R. v. Ammon, B. Kanellakopulos and R.D. Fischer, Chem. Phys. Lett., 2 (1968) 513; 4 (1970) 553.

18 D.G. Karraker and J.A. Stone, Inorg. Chem., 11 (1972) 1742.

19 R.D. Fischer, P. Laubereau and B. Kanellakopulos, Z. Naturforsch. A, 24 (1969) 616.

20 A.F. Reid, D.E. Scaife and P.C. Wailes, Spectrochem. Acta, 20 (1964) 1257.

21 B. Kanellakopulos in K.W. Bagnall (Ed.), Lanthanides and Actinides, Butterworths, London, 1972, p. 308.

22 R.D. Fischer and H.-D. Amberger, Proc. 10th Rare-earth Research Conf., Carefree, Ariz., May 1973, p. 15.

23 V.I. Kulishov, E.M. Brainina, N.G. Bokiy and Yu.T. Struchkov, J. Chem. Soc., Chem. Commun., (1970) 475;
V.I. Kulishov, N.G. Bokiy and Yu.T. Struchkov, Zh. Strukt. Khim., 11 (1970) 700.

24 J.L. Calderon, F.A. Cotton, B.G. DeBoer and J. Takats, J. Amer. Chem. Soc., 93 (1971) 3592.

25 V.I. Kulishov, E.M. Brainina, N.G. Bokiy and Yu.T. Struchkov, J. Organometal. Chem., 36 (1972) 333.

26 J.H. Burns, J. Amer. Chem. Soc., 95 (1973) 3815.

27 W.R. Busing and H.A. Levy, Acta Crystallogr., 10 (1957) 180.

28 P. Coppens and W.C. Hamilton, Acta Crystallogr. A, 26 (1970) 71.

29 D.T. Cromer and J.T. Waber, Acta Crystallogr., 18 (1965) 104.

30 D.T. Cromer, Acta Crystallogr., 18 (1965) 17.

31 W.C. Hamilton and J.A. Ibers, Acta Crystallogr., 17 (1964) 781.

32 W.C. Hamilton, Acta Crystallogr., 18 (1965) 502.

33 K.O. Hodgson and K.N. Raymond, Inorg. Chem., 12 (1973) 458.

34 R.G. Hayes and N. Edelstein, J. Amer. Chem. Soc., 94 (1972) 8688.

35 L.T. Reynolds and G. Wilkinson, J. Inorg. Nucl. Chem., 2 (1956) 246.

36 C.H. Wong, T. Yen and T. Lee, Acta Crystallogr., 18 (1965) 340.

37 C.H. Wong, T. Lee and Y. Lee, Acta Crystallogr. B, 25 (1969) 2580.

38 J.H. Burns, W.H. Baldwin and F.H. Fink, Amer. Cryst. Assoc. Gainesville Mtg. Abstr. No. D4, Jan. 1973.

39 L.J. Nugent, P.G. Laubereau, G.K. Werner and K.L. Vander Sluis, J. Organometal. Chem., 27 (1971) 365.

40 International Tables for X-ray Crystallography, Vol. 1, Kynoch Press, Birmingham, 1952, p. 211.