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The Crystal Structure of β-Tetrakis(acetylacetonato)-neptunium(IV)

BERT ALLARD

Departments of Inorganic Chemistry and Nuclear Chemistry, University of Göteborg and Chalmers University of Technology, P.O. Box, S-402 20 Göteborg 5, Sweden

The crystal structure of β-tetrakis(acetylacetonato)neptunium(IV), molecular formula $[Np(C_5H_7O_2)_4]$, has been determined by X-ray methods. The unit cell is monoclinic (space group $C2/c$) with the lattice parameters $a = 22.055$ Å, $b = 8.380$ Å, $c = 14.416$ Å, $\beta = 116.23°$, $V = 2390$ Å^3 and $Z = 4$. The structure has been solved from three-dimensional Patterson and electron density calculations. A least squares refinement of the structure, based on 1844 independent structure factors, gave a final R-value of 0.090.

The neptunium atom is coordinated by eight oxygen atoms in the form of a slightly distorted square antiprism (D_{4d}-$\bar{8}2m$), the mean value of the Np–O bond distances being 2.31 Å. The symmetry of the acetylacetonate ligand attachment around the antiprismatic inner coordination polyhedron is nearly D_2-222. The acetylacetonate ligand rings are not planar. The mean angle between the two planes O–Np–O and O–C–CH–C–O is 22.0°.

In connection with studies of complexes formed between tetravalent actinides and β-diketones, the acetylacetonate complex of neptunium(IV) has been synthesized and investigated. (In this report the acetylacetonate ligand is denoted by A, the complete molecule thus being NpA_4.)

Two different modifications of the tetravalent actinide acetylacetonates exist, and, previously, both the α- and β-modifications of ThA_4 and UA_4 have been investigated.[1,2] It was of interest to study the conditions for the formation of the α- and β-modifications of NpA_4. In this work, the synthesis and the crystal structure of the β-modification of NpA_4 have been investigated. Some results have already been presented in a preliminary report.[3]

EXPERIMENTAL

Preparation of the crystals. β-NpA_4 was prepared as described previously.[3] The effect of recrystallisation from different solvents at various temperatures has been studied. Light green, needle-shaped crystals of β-NpA_4 were formed at room temperature in aromatic solvents such as benzene or toluene. Sometimes crystals, which were probably

α-NpA_4, were formed in non-aromatic polar solvents, such as diethyl ether or acetone, usually below room temperature. The most stable modification at room temperature seems to be the β-modification. All experimental work was carried out in a sealed glove-box.

X-Ray methods. The structure investigation was based on single crystal X-ray diffraction measurements using multiple-film equi-inclination Weissenberg techniques. A crystal of the dimensions stated in Table 1 was mounted along the *c* axis, and Weissenberg

Table 1. Crystal dimensions. *d* (mm) is the distance to each face from an arbitrary origin inside the crystal.

Boundary face	*d*
1 0 0 −1 0 0	0.021
0 1 0 0 −1 0	0.104
0 0 1 0 0 −1	0.241

Crystal volume: 4.69×10^{-3} mm³.

photographs corresponding to $hk0-hk12$ were taken, using Cu$K\alpha$ radiation. The intensities were estimated by visual comparison with a standard scale made from timed exposures of a strong $hk0$ reflection. A correction for Lorentz and polarisation effects was performed with the program DATA P2,[4] after the intensities of the six films recorded for each layer line had been brought on to a common scale, using the least squares procedure of Hamilton, Rollett and Sparks.[4] The linear absorption coefficient of NpA_4 is 269.1 cm^{-1} for Cu$K\alpha$ radiation, calculated according to the method of Leroux.[5] No absorption correction was, however, performed until a preliminary structure had been found. The scale factors between the 13 layer lines were initially chosen in accordance with the exposure times.

In the preliminary structure investigation,[3] the crystals used for single crystal diffraction measurements disintegrated after about 6 h of X-ray irradiation. In the present investigation the crystals were, however, still intact after an irradiation of 300 h duration, which indicates that these crystals were probably purer than those obtained in the preliminary investigation. The crystals were mounted in 0.2 mm sealed glass capillaries without any kind of supporting matrix.

STRUCTURE DETERMINATION

Unit cell dimensions. The unit cell dimensions were obtained from X-ray powder photographs [3] taken in a Guinier focusing camera with Cu$K\alpha$ radiation, using potassium chloride as an internal standard. The unit cell is monoclinic with the lattice parameters:

$a = 22.055 \pm 0.005$ Å, $b = 8.380 \pm 0.001$ Å, $c = 14.416 \pm 0.001$ Å, $\beta = 116.23 \pm 0.01°$, $V = 2390$ Å³.

Space group and cell contents. In the Weissenberg photographs only reflections of the following types were observed:

hkl: $h+k=2n$, $h0l$: $l=2n$, $(h=2n)$, $0k0$: $(k=2n)$

The only possible space group is therefore No. 15, $C2/c$.[6]

The density of the crystals as measured by the flotation method using an aqueous solution of $ZnCl_2$ was found to be 1.77 g/cm³. The calculated density for a unit cell containing four formula units of NpA_4 is 1.76 g/cm³.

Determination of the atomic positions. The structure determination was based on 1844 independent reflections from the layers $hk0-hk12$. The positions of the neptunium atoms were deduced from a three-dimensional Patterson function $P(uvw)$ calculated with the program DRF.[4] Apart from those at (0,0,0) and ($\frac{1}{2}$,$\frac{1}{2}$,0) (relative height: 1000) the most dominant peaks appeared at (0,0.14,$\frac{1}{2}$) and ($\frac{1}{2}$,0.37,$\frac{1}{2}$) with relative heights of 450. Since there were no

Table 2. Atomic coordinates, expressed as fractions of unit cell edges, and anisotropic thermal parameters with their standard deviations (in parentheses) for β-NpA_4. The temperature factor is defined as follows:
$B = \exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.

(a) Positions

Atom	x	y	z
Np	0.0000	0.9324(1)	0.2500
O1	0.0623(7)	0.7179(18)	0.2410(14)
O2	0.1121(6)	0.0186(21)	0.3025(14)
O3	0.0507(8)	0.8452(17)	0.4175(13)
O4	0.0089(8)	0.1426(24)	0.3551(18)
C1	0.1390(17)	0.4958(30)	0.2884(34)
C2	0.1233(15)	0.6773(39)	0.2895(28)
C3	0.1784(13)	0.7805(38)	0.3460(25)
C4	0.1673(12)	0.9518(35)	0.3458(25)
C5	0.2292(17)	0.0597(46)	0.3980(36)
C6	0.1292(13)	0.8093(43)	0.5957(24)
C7	0.0881(13)	0.9058(27)	0.5059(27)
C8	0.0923(13)	0.0789(35)	0.5216(29)
C9	0.0534(13)	0.1815(32)	0.4514(25)
C10	0.0531(15)	0.3578(37)	0.4785(24)

(b) Temperature factors

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Np	0.048(0)	0.037(0)	0.039(1)	0.000	0.034(1)	0.000
O1	0.065(6)	0.040(7)	0.073(10)	0.033(13)	0.041(15)	−0.042(16)
O2	0.055(5)	0.063(9)	0.068(9)	−0.015(12)	0.076(16)	0.008(17)
O3	0.077(7)	0.037(7)	0.054(9)	−0.002(13)	0.055(16)	−0.001(13)
O4	0.065(6)	0.064(10)	0.110(13)	0.001(14)	0.102(22)	−0.028(22)
C1	0.135(18)	0.046(9)	0.145(30)	0.115(32)	0.058(41)	0.007(31)
C2	0.124(14)	0.068(16)	0.091(19)	0.094(31)	0.119(37)	0.019(35)
C3	0.069(12)	0.077(16)	0.070(18)	0.045(26)	0.032(26)	−0.020(31)
C4	0.052(9)	0.085(18)	0.071(18)	0.008(21)	0.046(24)	−0.006(28)
C5	0.065(14)	0.109(28)	0.114(30)	−0.028(32)	0.036(36)	0.007(43)
C6	0.067(11)	0.098(20)	0.065(17)	0.043(29)	0.050(26)	0.013(34)
C7	0.079(11)	0.048(11)	0.052(15)	0.005(17)	0.064(26)	0.018(21)
C8	0.079(10)	0.078(17)	0.088(19)	0.044(29)	0.095(34)	−0.027(31)
C9	0.053(11)	0.062(13)	0.089(19)	−0.016(21)	0.035(27)	−0.056(30)
C10	0.119(15)	0.065(15)	0.049(16)	0.032(28)	0.076(31)	−0.018(27)

other peaks of this order of magnitude, it was concluded that the four neptunium atoms in the unit cell must be situated in the position $C2/c$: $4e$, with $y_{Np} = 0.93$.

Table 3. Observed and calculated structure factors for β-NpA_4. The columns are h, $|F_o|$ and F_c, respectively.

h	0	0
-24	51	51
-22	82	73
-20	90	87
-18	151	141
-16	159	161
-14	158	160
-12	191	189
-10	208	205
-6	257	250
-4	232	219

h	-1	0
-23	56	55
-21	77	69
-19	103	93
-17	122	123
-15	120	110
-13	163	167
-11	241	223
-9	299	266
-7	278	229
-5	288	274
-3	293	291
-1	352	480

h	-2	0
-24	30	33
-22	40	38
-20	60	52
-18	72	67
-16	57	56
-14	87	87
-12	155	140
-10	250	185
-8	260	233
-6	188	171
-4	145	146
-2	125	129
0	182	199

h	-3	0
-19	23	26
-17	36	36
-13	37	37
-11	77	60
-9	95	82
-7	40	42
-5	42	34
-1	44	45

h	-4	0
-10	30	-31
-8	30	-19
-6	20	-21
-4	99	-93
-2	105	-97
0	39	-39

h	-5	0
-20	31	-31
-18	34	-35
-16	35	-33
-14	69	-59
-12	113	-89
-10	86	-77
-8	94	-86
-6	88	-89
-4	86	-91
-2	105	-115
0	115	-131

h	-6	0
-21	38	-38
-19	48	-48
-17	55	-52
-15	90	-81
-13	141	-123
-11	129	-126
-9	110	-105
-7	112	-117
-5	126	-143
-3	105	-120
-1	93	-108

h	-7	0
-17	57	-52
-15	60	-63
-13	87	-87
-11	111	-108
-9	119	-116
-7	116	-126
-5	113	-128
-3	107	-110
-1	123	-131

h	-8	0
-16	44	-53
-14	59	-60
-12	83	-79
-10	85	-81
-8	98	-88
-6	96	-97
-4	101	-109
-2	101	-108
0	102	-113

h	-9	0
-11	37	-38
-9	54	-43
-7	61	-57
-5	66	-68
-3	71	-75
-1	74	-83

h	-10	0
-6	29	-30
-4	35	-40
-2	35	-36
0	25	-30

h	-1	1
-25	22	-18
-21	23	-21
-19	46	-40
-17	65	-65
-15	57	-57
-13	72	-67
-11	78	-80
-9	45	-30
-7	65	-59
-5	36	-28
-3	102	-95
-1	197	-229
1	169	-161
3	114	-86
5	199	-161
7	91	-100
9	44	-35
11	81	-77
13	70	-64
15	73	-63
17	55	-51
19	37	-38
21	37	-33

h	-2	1
-24	48	-41
-22	51	-43
-20	63	-59
-18	84	-73
-16	85	-85
-14	86	-87
-12	147	-133
-10	139	-124
-8	165	-162
-6	228	-233
-4	256	-254
-2	236	-251
0	168	-173
2	162	-155
4	179	-184
6	208	-190
8	130	-110
10	192	-158
12	159	-144
14	121	-111
16	87	-85
18	72	-71
20	58	-60
22	47	-48

h	-3	1
-23	53	-53
-21	71	-70
-19	85	-84
-17	108	-93
-15	130	-121
-13	155	-148
-11	181	-170
-9	197	-194
-7	286	-272
-5	237	-259
-3	246	-270
-1	183	-200
1	211	-250
3	219	-244
5	239	-243
7	233	-222
9	210	-194
11	231	-181
13	143	-139
15	104	-107
17	83	-88
19	77	-81
21	52	-57

h	-4	1
-22	52	-56
-20	71	-76
-18	92	-92
-16	117	-125
-14	157	-150
-12	181	-159
-10	161	-156
-8	211	-218
-6	213	-227
-4	204	-216
-2	246	-258
0	281	-287
2	300	-291
4	201	-215
6	224	-223
8	191	-186
10	177	-168
12	152	-139
14	120	-127
16	100	-105
18	74	-84
20	50	-57

h	-5	1
-21	52	-50
-19	72	-67
-17	83	-78
-15	109	-100
-13	161	-140
-11	151	-142
-9	135	-120
-7	176	-187
-5	179	-189
-3	174	-181
-1	180	-186
1	183	-189
3	183	-187
5	199	-201
7	145	-141
9	119	-113
11	152	-135
13	124	-110
15	86	-85
17	62	-66
19	45	-50

h	-6	1
-20	22	-30
-18	33	-40
-16	41	-46
-14	61	-56
-12	103	-91
-10	90	-93
-8	86	-97
-6	91	-105
-4	76	-81
-2	69	-78
0	75	-80
2	82	-93
4	90	-123
6	131	-125
8	75	-80
10	94	-83
12	77	-62
14	47	-44
16	39	-36
18	29	-27

h	-7	1
-3	32	-21
1	22	-21
3	29	-26
5	39	-37

h	-8	1
-10	35	35
-8	34	31
-6	32	29
-4	30	22
0	34	27
2	30	22
4	36	31
6	43	42
8	46	43

h	-9	1
-13	26	33
-11	43	44
-9	53	55
-7	47	51
-5	52	50
-3	60	59
-1	65	66
1	58	62
3	57	54
5	56	53
7	53	58
9	52	52
11	29	36

h	-10	1
-8	36	49
-6	46	54
-4	49	62
-2	58	66
0	59	67
2	61	68
4	56	62
6	44	54

h	0	2
-24	68	-60
-22	72	-68
-20	104	-102
-18	152	-145
-16	145	-139
-14	221	-188
-12	225	-213
-10	280	-272
-8	423	-400
-6	458	-493
2	155	-144
4	239	-250
6	218	-268
8	206	-248
10	192	-211
12	170	-170
14	133	-137
16	150	-154
18	98	-95

h	-1	2
-25	44	-48
-23	60	-57
-21	86	-73
-19	124	-121
-17	130	-121
-15	139	-131
-13	183	-172
-11	246	-221
-9	340	-259
-7	354	-333
-5	376	-382
-3	249	-312
-1	229	-370
1	164	-182
3	324	-300
5	281	-264
7	236	-236
9	209	-203
11	175	-177
13	115	-117
15	113	-119
17	114	-112
19	68	-67

h	-2	2
-24	32	-33
-22	47	-41
-20	74	-69
-18	85	-88
-16	96	-84
-14	104	-97
-12	113	-95
-10	219	-193
-8	201	-178
-6	172	-167
-4	140	-139
-2	236	-234
0	217	-213
2	147	-153
4	188	-180
6	277	-239
8	225	-199
10	108	-101
12	90	-92
14	81	-72
16	84	-76
18	66	-61
20	46	-46

h	-3	2
-19	35	-42
-17	48	-48
-15	47	-38
-13	44	-29
-11	59	-52
-9	70	-64
-7	39	-23
-5	53	-43
-3	62	-63
-1	155	-163
1	106	-120
3	86	-87
5	86	-78
7	120	-95
9	66	-50
11	32	-27
15	37	-35
17	37	-40
19	28	-27

h	-4	2
-10	53	49
-8	76	63
-6	113	108
-4	110	118
-2	23	20
0	74	70
4	28	26
6	23	23
8	36	36
10	35	29

h	-5	2
-21	31	30
-19	43	41
-17	75	65
-15	107	93
-13	82	66
-11	57	46
-9	77	75
-7	90	92
-5	95	99
-3	105	110
-1	109	121
1	121	126
3	112	120
5	115	117
7	108	100
9	54	40
11	48	39
13	60	65
15	51	53
17	41	40
19	35	33

h	-6	2
-20	48	46
-18	67	66
-16	87	82
-14	125	101
-12	108	95
-10	82	80
-8	89	88
-6	132	131
-4	134	142
-2	125	131
0	122	129
2	156	169
4	176	185
6	112	115
8	102	90
10	79	81
12	75	79
14	51	64
16	49	60
18	40	49

h	-7	2
-19	43	50
-17	60	60
-15	84	77
-13	110	90
-11	96	93
-9	107	110
-7	138	145
-5	117	135
-3	104	115
-1	108	124
1	101	115
3	125	136
5	139	146
7	123	126
9	113	106
11	97	93
13	68	74
15	53	61

h	-8	2
-16	53	55
-14	69	64
-10	96	84
-8	100	91
-6	112	112
-4	107	112
-2	102	107
0	102	103
4	112	109
6	95	91
10	77	80
12	53	66
14	47	53

h	-9	2
-13	39	49
-11	52	48
-9	58	58
-7	65	67
-5	72	71
-3	72	71
-1	75	75
1	69	71
3	69	65
5	65	58
7	57	55
9	41	45

h	-10	2
-6	25	31
-4	35	35
-2	35	32
0	30	26

Table 3. Continued.

h -1 3		
-25	20	21
-23	26	26
-21	30	27
-19	43	41
-17	66	62
-15	72	69
-13	88	82
-11	61	52
-9	119	101
-7	178	155
-5	78	71
-3	105	156
-1	197	270
1	132	149
3	102	100
5	142	110
7	90	72
9	96	90
11	67	65
13	73	71
15	77	77
17	58	52
19	31	30

h -2 3		
-26	31	33
-24	49	44
-22	66	57
-20	74	60
-18	85	75
-16	97	95
-14	144	137
-12	202	159
-10	190	170
-8	281	259
-6	260	238
-4	158	198
-2	139	165
0	161	188
2	173	185
4	254	251
6	220	202
8	214	184
10	176	166
12	113	121
14	100	106
16	80	81
18	64	59
20	48	45

h -3 3		
-25	44	47
-23	61	58
-21	86	82
-19	102	89
-17	123	105
-15	131	128
-13	204	171
-11	206	181
-9	246	236
-7	258	262
-5	310	305
-3	261	258
-1	176	197
1	191	221
3	213	232
5	246	249
7	196	195
9	210	189
11	164	163
13	112	130
15	79	89
17	72	80
19	60	61
21	38	47

h -4 3		
-24	43	46
-22	63	60
-20	85	81
-18	118	105
-16	146	132
-14	189	155
-12	175	157
-10	184	172
-8	208	200
-6	197	192
-4	253	251
-2	245	244
0	259	260
2	236	233
4	216	229
6	183	180
8	158	145
10	130	133
12	125	119
14	101	100
16	77	82
18	68	70
20	44	49
22	39	40

h -5 3		
-21	56	54
-19	76	70
-17	89	87
-15	133	117
-13	146	144
-11	115	105
-9	125	119
-7	150	149
-5	150	153
-3	168	165
-1	174	173
1	175	174
3	196	193
5	179	170
7	93	95
9	106	103
11	97	96
13	67	73
15	60	62
17	55	57
19	39	44

h -6 3		
-22	19	28
-20	28	34
-18	36	44
-16	47	49
-14	61	57
-12	63	58
-10	58	57
-8	91	98
-6	102	102
-4	101	100
-2	104	102
0	85	88
2	75	73
4	91	85
6	71	61
8	75	68
10	87	69
12	45	42
14	39	39
16	35	35
18	21	25

h -7 3		
-7	32	35
-5	24	24
-1	32	26
1	23	16

h -8 3		
-6	26	-29
-4	31	-28
-2	36	-35
0	26	-31
2	26	-25
6	32	-24

h -9 3		
-13	29	-31
-11	41	-41
-9	43	-48
-7	47	-45
-5	51	-47
-3	60	-58
-1	67	-67
1	63	-61
3	51	-50
5	49	-46
7	42	-46
9	29	-35

h -10 3		
-8	44	-47
-6	51	-56
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9	65	-70
11	65	-67

h	-2	10
-26	25	-25
-24	52	-47
-22	61	-57
-20	66	-59
-18	75	-61
-16	100	-73
-14	96	-88
-12	93	-85
-10	95	-88
-8	128	-122
-6	142	-141
-4	123	-116
-2	94	-96
0	79	-79
2	91	-87
4	75	-78
6	70	-72
8	61	-62
10	51	-51
12	42	-44

h	-3	10
-25	17	-14
-23	20	-24
-21	23	-23
-15	30	-23
-13	41	-39
-11	33	-29
-7	47	-48
-5	59	-59
-3	55	-53
-1	39	-42
1	40	-34
3	40	-29

h	-4	10
-20	24	20
-18	31	25
-10	30	25
-8	55	48
-6	35	33

h	-5	10
-23	15	17
-21	21	24
-19	46	47
-17	59	57
-15	60	52
-13	60	49
-11	65	56
-9	81	75
-7	78	73
-5	63	56
-3	63	61
-1	65	60
1	57	56
3	69	57
5	49	46
7	39	39
9	30	33

h	-6	10
-22	24	33
-20	43	44
-18	53	59
-16	66	66
-14	65	61
-12	66	65
-10	76	77
-8	92	95
-6	89	93
-4	75	72
-2	76	74
0	84	82
2	90	77
4	71	63
6	59	58
8	46	49

h	-7	10
-19	44	53
-17	57	56
-15	59	52
-13	65	55
-11	78	74
-9	96	88
-7	100	96
-5	101	95
-3	91	85
-1	87	80
1	77	71
3	70	62
5	57	59

h	-8	10
-16	31	47
-14	53	50
-12	59	58
-10	66	64
-8	65	63
-6	68	65
-4	69	66
-2	68	67
0	67	66
2	55	60

h	-1	11
-23	20	20
-21	27	27
-19	35	39
-17	48	49
-15	55	53
-13	70	65
-11	62	56
-9	28	29
-7	32	37
-5	44	46
-3	46	41
-1	80	68
1	81	74
3	74	65
5	56	53
7	31	32
9	22	24

h	-2	11
-26	19	29
-24	27	36
-22	39	46
-20	50	55
-18	66	71
-16	86	79
-14	92	89
-12	99	98
-10	94	102
-8	99	109
-6	108	110
-4	80	81
-2	91	81
0	121	103
2	101	95
4	87	87
6	76	75
8	62	62
10	52	50

h	-3	11
-25	38	44
-23	52	53
-21	63	68
-19	87	88
-17	113	95
-15	108	96
-13	105	104
-11	116	113
-9	135	133
-7	131	132
-5	135	130
-3	130	126
-1	126	124
1	119	112
3	112	101
5	92	89
7	79	78
9	62	63

h	-4	11
-24	37	46
-22	51	54
-20	69	76
-18	99	95
-16	87	84
-14	97	94
-12	113	112
-10	125	124
-8	122	125
-6	123	124
-4	129	130
-2	132	130
0	122	114
2	105	96
4	94	90
6	74	74
8	57	61
10	42	50

h	-5	11
-23	29	40
-21	33	41
-19	51	58
-17	73	70
-15	67	67
-13	88	84
-11	106	101
-9	110	109
-7	114	111
-5	101	97
-3	85	82
-1	95	88
1	74	74
3	72	64
5	66	63
7	51	54

h	-6	11
-22	15	26
-20	20	30
-18	32	37
-16	31	37
-14	35	39
-12	47	50
-10	60	53
-8	61	57
-6	75	64
-4	55	52
-2	48	48
0	63	52
2	45	35
4	32	33
6	33	35

h	-8	11
-4	22	-22

h	0	12
-26	36	48
-24	60	71
-22	64	72
-20	73	75
-18	100	95
-16	120	118
-14	143	142
-12	131	150
-6	105	124
-4	108	125
-2	131	140
0	115	132
2	107	108
4	94	101
6	81	85

h	-1	12
-25	49	57
-23	61	68
-21	64	68
-19	71	70
-17	96	89
-15	134	112
-13	150	125
-11	108	107
-9	108	108
-7	141	135
-5	150	131
-3	137	126
-1	134	123
1	103	104
3	86	85
5	79	80
7	64	64

h	-2	12
-24	31	40
-22	33	44
-20	39	44
-18	44	45
-16	73	68
-14	97	86
-12	83	79
-10	73	70
-8	90	89
-6	107	100
-4	108	96
-2	85	75
0	71	66
2	66	66
4	64	59
6	53	52
8	45	44

h	-3	12
-15	44	40
-13	61	51
-11	32	30
-9	21	20
-7	33	32
-5	40	37
-3	32	26
-1	35	29
3	40	36
5	29	29
7	19	19

h	-5	12
-19	29	-36
-17	34	-35
-15	45	-42
-13	66	-55
-11	64	-56
-9	45	-44
-7	36	-31
-5	46	-41
-3	61	-57
-1	62	-53
1	56	-49
3	43	-40
5	31	-30

h	-6	12
-20	22	-32
-18	36	-41
-16	52	-48
-14	67	-62
-12	78	-73
-10	81	-73
-8	80	-72
-6	74	-67
-4	68	-63
-2	77	-69
0	76	-64
2	54	-52
4	42	-44

h	-7	12
-17	30	-45
-15	45	-51
-13	63	-63
-11	74	-71
-9	82	-72
-7	79	-71
-5	78	-69
-3	73	-67
-1	71	-63
1	43	-50

h	-8	12
-10	40	-49
-8	50	-53
-6	51	-57

The positions of the light atoms, *i.e.* oxygen and carbon, were deduced from a three-dimensional electron density difference synthesis calculated with the program DRF.[4] All oxygen and carbon atoms occupy positions $C2/c$: 8*f*. The positions of the hydrogen atoms were not determined.

Structure refinement. The structure was refined by a series of structure factor least squares cycles using the program BLOCK.[4] The scattering factors given by Cromer and Waber[7] were used for neptunium and those of Doyle and Turner[8] for oxygen and carbon, and the structure factors were weighted according to the formula $w=(a+|F_o|+c|F_o|^2)^{-1}$ suggested by Cruickshank,[9] with $a=40.0$ and $c=0.004$. An initial refinement of the parameters of neptunium only yielded a reliability index, $R=\sum||F_o|-|F_c||/\sum|F_o|$, of 0.22, which illustrates the scattering dominance of the neptunium atoms in the formula unit. Refinement of the parameters of neptunium, oxygen, and carbon, assuming isotropic temperature vibrations, gave $R=0.15$. After the introduction of absorption factors calculated with the program DATA P2[4] (the transmission factors varied from 0.04 to 0.39) an R-value of 0.11 was obtained. Finally, when allowance was made for anisotropic thermal vibrations of the atoms, the R-value converged to 0.090. The corresponding parameters are given in Table 2 and the observed and calculated structure factors are listed in Table 3.

An attempt to introduce corrections for secondary extinction and anomalous scattering[10] in the refinements gave no significant improvement.

Table 4. Distances (Å) and angles (°) for β-NpA_4 with standard deviations (in parentheses). The notation is in accordance with Fig. 1.

(a) Ligand 1.

	Distance		Angle
Np – O1	2.300(14)	O1 – Np – O2	71.9(1.0)
Np – O2	2.356(16)	Np – O1 – C2	134.3(1.6)
O1 – C2	1.266(36)	Np – O2 – C4	133.3(1.7)
O2 – C4	1.231(32)	O1 – C2 – C3	126.0(2.6)
C2 – C3	1.418(43)	O2 – C4 – C3	125.2(2.5)
C4 – C3	1.456(42)	C2 – C3 – C4	120.0(2.5)
C2 – C1	1.561(42)	O1 – C2 – C1	116.5(2.7)
C4 – C5	1.529(47)	O2 – C4 – C5	116.7(2.5)
O1 – O2	2.735(22)	C1 – C2 – C3	117.6(2.8)
Np – C3	3.761(40)	C3 – C4 – C5	118.0(2.5)

(b) Ligand 2.

	Distance		Angle
Np – O3	2.286(15)	O3 – Np – O4	71.7(1.1)
Np – O4	2.275(20)	Np – O3 – C7	136.5(1.3)
O3 – C7	1.278(30)	Np – O4 – C9	133.4(1.5)
O4 – C9	1.340(34)	O3 – C7 – C8	121.1(2.4)
C7 – C8	1.465(33)	O4 – C9 – C8	124.6(2.4)
C9 – C8	1.315(39)	C7 – C8 – C9	123.7(2.9)
C7 – C6	1.454(38)	O3 – C7 – C6	122.7(2.1)
C9 – C10	1.528(40)	O4 – C9 – C10	114.6(2.4)
O3 – O4	2.671(23)	C6 – C7 – C8	116.2(2.5)
Np – C8	3.739(35)	C8 – C9 – C10	120.8(2.6)

Thus, the observed structure factors calculated from visually estimated intensities are not sufficiently accurate to permit correction for these effects.

The distances and angles between adjacent atoms were calculated with the program DISTAN;[4] (*cf.* Table 4.)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The neptunium atom is coordinated by eight oxygen atoms in the form of a distorted square antiprism (D_{4d}-$\bar{8}2m$). The symmetry of the ligand attachment around the inner coordination polyhedron is close to D_2-222, (*cf.* Fig. 1). The ring skeletons, excluding the neptunium atom, are essentially planar. The ligand rings are, however, inclined at a mean angle of 22.0° for the two different ligands to the corresponding O – Np – O planes.

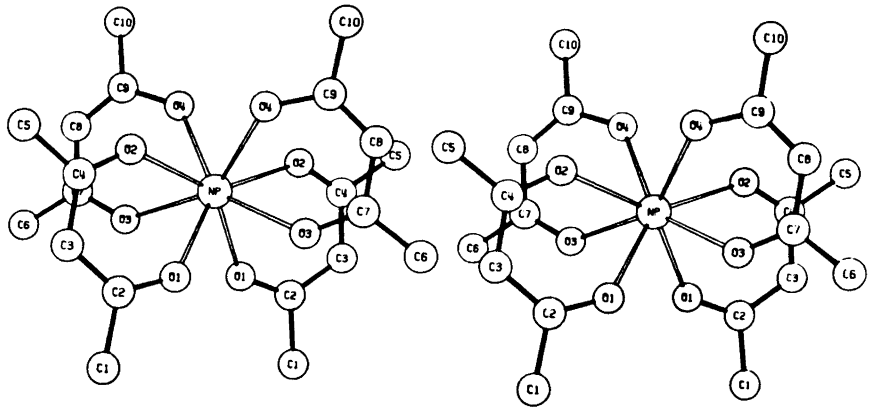

Fig. 1. The β-NpA_4 formula unit (stereoscopic drawing).

The rectangular faces of the antiprism are essentially parallel and planar, the deviations from the mean plane being less than 0.002 Å for the four oxygen atoms.

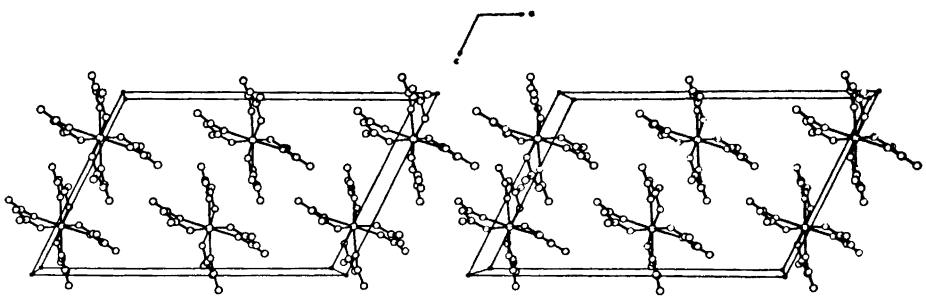

Fig. 2. The unit cell of β-NpA_4 (stereoscopic drawing).

The packing of the molecules in crystalline β-NpA_4 is illustrated in Fig. 2. The ring folding is apparently due to packing relations between the molecules. The closest intermolecular distance between non-bonded atoms is 3.53 Å (C7 – C9) and between methyl groups 3.71 Å (C1 – C6).

It is possible to obtain some information about the character of the bonds within the ligand rings by comparing the bond distances with the values for C – C (1.537 Å), C = C (1.337 Å), C⋯C in benzene (1.394 Å), C – O (1.426 Å), and C = O in ketones (1.215 Å) given in *Tables of Interatomic Distances and Configuration in Molecules and Ions* [11] (*cf.* Table 4). The C1 – C2 and C4 – C5 distances of ligand 1 are equal within the standard devation σ, and the mean value of the distances is 1.55 Å. The corresponding distances for ligand 2, C6 – C7 and C9 – C10, are equal within 2σ, the mean value being 1.49 Å. For the whole molecule the mean value is 1.52 Å. These distances, which correspond to C – CH_3 bonds, seem to be single bonds, as might be expected.

The difference between the C2 – C3 and C3 – C4 distances of ligand 1 is less than σ, the mean value of the bonds being 1.44 Å. These C – CH bonds can neither be described as double nor single but would seem to be rather close to the bonds of benzene. The corresponding bond distances for ligand 2, C7 – C8 and C8 – C9, deviate from each other by more than 3σ, the mean value being 1.39 Å.

The O – C distances of ligand 1, *i.e.* O1 – C2 and O2 – C4, are equal within σ, with a mean value of 1.25 Å. This value indicates a bond very close to a double bond. In ligand 2 the difference between O4 – C9 and O3 – C7 is greater than 2σ, and the mean value of the bonds is 1.30 Å.

Because of the differences between corresponding bonds in ligand 2 there are large angle deviations, especially between O3 – C7 – C6 and O4 – C9 – C10, where the difference is greater than 3σ.

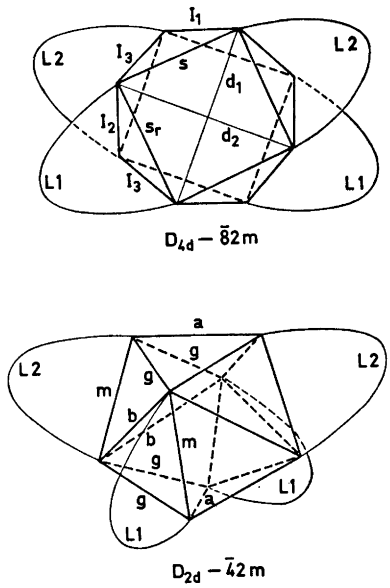

Fig. 3. Comparison of the two extreme coordination polyhedra, the square antiprism (D_{4d}-$\bar{8}2m$) and the dodecahedron (D_{2d}-$\bar{4}2m$). L1 = ligand 1, L2 = ligand 2.

Thus ligand 1 seems to be bisymmetrical, as might be expected, indicating resonance stabilization of the ligand rings caused by electron delocalization. Ligand 2 differs considerably from ligand 1, and there seem to be significant deviations from the expected bisymmetry. The same kind of deviations have been reported to occur in β-UA_4 by Titze.[2]

There are two coordination polyhedra which are almost equally probable from a theoretical point of view.[12] These isomers are the square antiprism and the dodecahedron; (*cf.* Fig. 3). The main factors determining the choice of polyhedron are the geometrical constraints, largely controlled by the stereochemical character of the ligands, and the mutual closed-shell repulsion of the atoms constituting the inner coordination group. Minimization of the ring constraint leads to a rather constant, well-defined ring span, which seems to be independent of the central atom, as can be seen in Tables 5 and 6. The

Table 5. Mean distances (Å) in the square antiprisms of different acetylacetonate complexes with standard deviations (in parentheses). Some of the original values have been recalculated; (*cf.* Fig. 3).

	β-ZrA_4 [13]	β-CeA_4 [14]	β-UA_4 [2]	β-NpA_4
s_r	2.67(1)	2.71(5)	2.68(4)	2.71(2)
s	2.59(1)	2.79(6)	2.80(4)	2.78(2)
l_1	2.69(2)	2.93(5)	2.91(7)	2.87(3)
l_2	2.81(1)	2.99(5)	3.00(4)	2.94(2)
l_3	2.72(1)	2.91(6)	2.93(5)	2.88(2)
d_1	3.78(2)	3.98(6)	3.92(5)	3.90(3)
d_2	3.66(2)	3.79(6)	3.83(5)	3.87(3)

Table 6. Parameters for different acetylacetonate complexes. (For the ring folding of β-CeA_4 and β-UA_4 other values are given by Titze.[2,14] These values have been recalculated.)

	β-ZrA_4 [13]	β-CeA_4 [14]	β-ThA_4 [1,15]	β-UA_4 [2]	β-NpA_4
Ionic radius (Å) [16]	0.79	0.94	1.02	0.97	0.95
Cell volume (Å^3)	2286	2386	2446	2411	2390
M–O (Å)	2.20	2.32	2.41	2.32	2.31
O–M–O[a] (°)	75.0	71.3		71.6	71.8
Angle sum, L1 (°)	710.2	708.5		704.7	710.7
Angle sum, L2 (°)	711.5	710.7		712.6	711.0
Ring folding, L1 (°)	23.7	25.1		25.8	22.5
Ring folding, L2 (°)	22.7	22.2		21.6	21.5

[a] The angle within one ligand is intended.

preservation of the O–M–O bond angle is attributable mostly to the maintenance of the ring geometry and not to the bond-directing capacity of the metal atom.

Minimization of the ligand repulsive energy for either of the two extreme coordination polyhedra leads to shape parameters which differ significantly from those of the hard sphere model.[12] One way of determining the type of coordination polyhedron and the degree of hybridization between the two isomers is to compare the measured bond distances with the calculated parameters of the theoretically most favourable polyhedron. The discrepancies from the ideal antiprism are in such a direction as to indicate a certain degree of dodecahedral hybridization.

For all the acetylacetonate complexes compared the diagonals of the rectangular faces of the antiprism are unequal with d_1 greater than d_2 (*cf.* Table 5). In Table 7 the theoretically calculated distances of the most favour-

Table 7. Comparison between the calculated distances for the most favourable coordination polyhedron [12] and the measured distances for different acetylacetonate complexes; (*cf.* Fig. 3). The percentage deviations from the calculated values (index *c*) are given.

a) Square antiprism

	β-ZrA_4	β-CeA_4	β-UA_4	β-NpA_4
d_c-d_1	−2.2	3.6	4.9	4.4
d_c-d_2	1.1	8.2	7.0	5.1
l_c-l_1	2.9	−0.3	0.0	0.7
l_c-l_2	−1.4	−2.4	−3.1	−1.8
l_c-l_3	1.8	0.3	−0.7	−1.4
s_c-s	1.1	−1.1	−1.8	−1.4
s_c-s_r	−1.9	1.8	2.5	1.1

(b) Dodecahedron

	β-ZrA_4	β-CeA_4	β-UA_4	β-NpA_4
a_c-l_1	−4.7	−7.7	−7.4	−6.7
b_c-l_2	14.3	13.6	12.8	14.3
g_c-l_3	0.4	−1.0	−2.4	−1.1
g_c-s	5.1	3.8	2.1	2.5
m_c-s_r	−3.9	0.4	1.1	0.7

able polyhedra are compared with the measured distances. The standard deviations of the distances are too large to allow a quantitative analysis of the deviations. There seems, however, to be a significant difference between the zirconium complex and the other three complexes, possibly due to the difference in M−O bond distances. All the complexes show dodecahedral elements.

Comparison between the most accurate values, *i.e.* for β-ZrA_4 and β-NpA_4, gives indication as to an increased degree of dodecahedral hybridization with increasing ionic radius. This is valid for d_1, d_2, s and especially for s_r, which is fixed by the ring constraint. For l_2 and l_3 the differences are not significant. On the other hand, l_1 seems to fit the antiprism better for β-NpA_4 than for β-ZrA_4.

The observed stabilities of the complexes at room temperature decrease in the order β-$ZrA_4 \geq \beta$-CeA_4, β-UA_4, β-$NpA_4 > \beta$-ThA_4 and α-$ThA_4 \geq \alpha$-CeA_4, α-UA_4, α-$NpA_4 > \alpha$-ZrA_4. On the other hand, for complexes with the same central atom the order is β-$ZrA_4 > \alpha$-ZrA_4, and α-$ThA_4 > \beta$-ThA_4. An increase in the M – O bond distance seems to stabilize the α-form in comparison with the β-form.

It would be interesting to study the effect of an increase in the M – O bond distance within the lanthanide and actinide series, *e.g.* in the thorium complex, and to compare the structures of the α- and β-modifications. It may be possible that the α-modification can be described as being dodecahedral with considerable antiprismatic features. The structure data on the α-modification published hitherto [17,18] are not, however, sufficiently accurate to establish this point. The author intends to investigate the crystal structure of α-ThA_4 in the near future.

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