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Structural Studies on the Rare Earth Carboxylates

19. The Crystal and Molecular Structure of Penta-aquo Tris-malonato Di-europium(III) Trihydrate

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The crystal structure of $Eu_2(C_3H_2O_4)_3.8H_2O$ has been determined from three-dimensional, photographic, X-ray intensity data. The crystals are orthorhombic, belong to the space group *Pnma*, and the cell parameters are $a = 12.220(5)$ Å, $b = 8.100(3)$ Å, and $c = 20.545(9)$ Å. $Z = 4$.

There are two non-equivalent europium ions and three non-equivalent malonate ions in the structure. They are linked to europium-malonate layers which are in turn held together by hydrogen bonds *via* water molecules between the layers.

One europium ion is coordinated by eight oxygens forming a distorted square antiprism and the other by nine oxygens forming a distorted tricapped trigonal prism. The average Eu – O bond distances are 2.42 Å and 2.51 Å, respectively.

The malonate ions possess mirror-symmetry, and the two carboxylate groups are in each ion twisted in the same direction out of the carbon chain plane. The twist angles are in the range 30 – 50°. The malonate ions form six-membered chelate rings with europium. Two of these rings have a boat conformation while the third ring adopts a chair conformation.

There are two different types of lanthanoid malonates of the composition $M_2mal_3.8H_2O$ (M = lanthanoid, mal = $OOC.CH_2COO^{2-}$); one with M = Ce – Gd and the other with M = Eu – Lu. The lighter lanthanoids also form a metastable hexahydrate, $M_2mal_3.6H_2O$.

The structure of the compounds $Nd_2mal_3.8H_2O$ and $Nd_2mal_3.6H_2O$ have been reported previously.[1,2] This paper deals with the structure of the heavier lanthanoid malonates represented by the europium compound $Eu_2mal_3.8H_2O$ (EUM).

The investigation of these structures was undertaken in order to study the coordination geometry around the lanthanoid ions and the conformation of the malonate ion in lanthanoid malonate complexes. The possible influence

of the lanthanoid contraction on the malonate ligands is also of interest. For the latter purpose it would have been more convenient to choose the isotypic compound formed by the smallest lanthanoid ion for the present study. However, the crystal quality which is poor for all the compounds becomes worse through the series and suitable single crystals could be prepared only of EUM.

The L_{II} absorption edge of europium lies just above $\lambda_{CuK\alpha}$ and hence the mass absorption coefficient of europium for Cu$K\alpha$-radiation is large and inaccurately known.[3] To avoid this disadvantage attempts were made to record the intensity material using Mo$K\alpha$-radiation. With the small crystals available the time of exposure needed was found to be at least 72 h per layer. During this long exposure the crystals disintegrated even when sealed in a glass capillary.

The possibility of using Cu$K\alpha$-radiation in spite of the large absorption was then considered. The influence of absorption errors in structure determinations has been studied by Werner [4] and by Srivastava *et al.*[5] Judging from their work the study of the small, needle shaped crystals of EUM using Cu$K\alpha$-radiation could be expected to give reliable information on the main features of the structure such as the coordination number of the europium ion, the type of coordination polyhedron formed around it, and the approximate conformation of the malonate ion. Since this information was considered valuable, it was decided to study the structure using Cu$K\alpha$-radiation.

EXPERIMENTAL

The method of preparation and the habit of the crystals of EUM were described in Ref. 1. They rapidly disintegrate when exposed to X-radiation and to prevent this they were sealed in Lindemann glass capillaries.

A crystal of the dimensions $0.16 \times 0.02 \times 0.04$ mm^3, mounted along the 0.16 mm edge, was used in recording the layers $h0l - h6l$ with the non-integrated Weissenberg, multi-film technique. Ni-filtered Cu-radiation was used.

The intensities of 692 independent reflexions were measured visually by comparison with a calibrated scale. Most of them, 650 reflexions, had $\sin\theta/\lambda \leq 0.5$. Thus 60 % of the possible reflexions within this limit were measured while only 20 % of the reflexions in the whole of the investigated region had measurable intensity. The data were corrected for Lorentz and polarisation effects.

An approximate value of the mass absorption coefficient of europium for Cu$K\alpha$-radiation is given in International Tables, Vol. III, 1st Ed. This value has been excluded in the 2nd Ed. since it was considered too unreliable. Nevertheless, it was used in an attempt to apply an approximate correction for absorption effects to the data (see below). The linear absorption coefficient of EUM used was 443 cm^{-1} and the transmission factors evaluated by numerical integration were then in the range $0.17 - 0.50$.

The powder photographs were taken at room temperature in a Guinier-Hägg focusing camera with Cu$K\alpha$-radiation ($\lambda = 1.54178$ Å). Lead nitrate (cubic $a = 7.857$ Å) was used as internal standard.

UNIT CELL AND SPACE GROUP

EUM crystallizes in the Laue class *mmm*. The systematically absent reflexions are $0kl$: $k+l \neq 2n$ and $hk0$: $h \neq 2n$. The possible space groups are then $Pna2_1$ and $Pnma$. The structure was assumed to be centrosymmetric

and the subsequent calculations did not contradict this assumption. Thus the space group is *Pnma* (No. 62).[6]

The unit cell dimensions were determined from powder data by least squares refinement as described before.[7] The observed powder pattern is given in Table 1 and the final cell parameters are $a = 12.220(5)$ Å, $b = 8.100(3)$ Å, and $c = 20.545(9)$ Å. $Z = 4$.

Table 1. Powder data for the compound $Eu_2(C_3H_2O_4)_3.8H_2O$. Observed and calculated values of $10^5\sin^2\theta$ are given together with the observed powder intensities.

h k l	obs	calc	I_{obs}	*h k l*	obs	calc	I_{obs}
1 0 1	537	539	s	2 1 5	6013	6018	vvw
0 0 2	560	563	s	4 0 0	6364	6368	vvw
1 0 2	960	961	vvw	4 0 1	6505	6509	w
1 1 1	1443	1445	vw	3 1 4	6751	6741	w
1 0 3	1665	1665	w	3 1 5	8017	8008	w
1 1 2	1866	1867	m	0 2 6	8697	8692	vvw
2 0 2	2148	2155	vvw	1 3 2	9115	9114	m
0 0 4	2240	2253	w	3 2 4	9465	9458	w
2 1 0	2498	2498	vvw	2 3 1	9899	9885	m
1 1 3	2567	2571	vvw	4 2 0	10018	9991	vw
2 1 1	2637	2639	s	2 2 6	10331	10284	vvw
2 1 2	3058	3061	vw	4 1 5	10817	10794	vvw
1 1 4	3547	3557	vvw	0 3 5	11691	11673	w
0 2 0	3640	3623	vvw	3 3 1	11847	11875	vvw
3 0 1	3713	3723	vvw	1 3 5	12046	12071	vvw
1 2 1	4177	4162	m	0 1 9	12282	12311	w
0 2 2		4187		0 2 8	12653	12635	vw
0 1 5	4431	4426	w	3 3 3	12995	13002	vw
1 2 2	4588	4585	m	1 2 8		13033	
3 0 3	4840	4849	m	2 3 5	13255	13265	vw
3 1 2	5054	5051	w	3 3 4	13954	13987	vvw
0 0 6		5069		0 4 0	14471	14494	w
1 2 3	5290	5289	m	5 2 3	14817	14841	vw
				4 2 6	15082	15060	vvw

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The structure of EUM was determined by the heavy atom method. The three-dimensional Patterson synthesis showed the presence of two non-equivalent europium ions. They are situated in the mirror planes, *i.e.* in the positions 4*c*. From the first electron density difference synthesis it was possible to select the positions of the remaining non-hydrogen atoms except for half a water oxygen per asymmetric unit.

The deduced parameters were improved by full-matrix, least squares refinement. The discrepancy indexes $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{\frac{1}{2}}$ converged to 0.124 and 0.154, respectively. The electron density maps of the following difference synthesis showed a peak interpretable as a water oxygen at (0.02, 0.42, 0.50). Half an oxygen at this position was included in the following refinement of the atomic coordinates,

isotropic temperature factors and inter-layer scale factors, resulting in $R = 0.124$ and $wR = 0.152$.

At this stage the data were corrected for absorption using the approximate mass absorption coefficient of europium given in International Tables, Vol. III, 1st Ed. This treatment had the following effect: The values of R and wR decreased to 0.091 and 0.116, respectively, and the estimated standard deviations, σ, were reduced by about 25 %. The shifts in the positional parameters were less than σ except for $\Delta x_{O(5)}$ and $\Delta z_{O(6)}$ which were less than 2σ.

Table 2. Analysis of the weighting scheme $w = 1/(1.00 + |F_o| + 0.004|F_o|^2 + 0.00005|F_o|^3)$. The averages $\overline{w\Delta^2}$, where $\Delta = |F_o| - |F_c|$, are normalized.

Interval $\|F_o\|$	Number of reflexions	$\overline{w\Delta^2}$	Interval sin θ	Number of reflexions	$\overline{w\Delta^2}$
0 – 52	67	0.96	0.00 – 0.33	85	1.34
52 – 61	69	0.95	0.33 – 0.41	80	1.03
61 – 69	69	0.89	0.41 – 0.47	62	0.85
69 – 76	69	1.17	0.47 – 0.52	69	0.67
76 – 86	70	1.09	0.52 – 0.56	58	0.88
86 – 98	69	1.08	0.56 – 0.59	54	1.25
98 – 114	69	1.13	0.59 – 0.62	47	1.19
114 – 136	69	1.17	0.62 – 0.65	43	0.94
136 – 172	69	0.79	0.65 – 0.68	34	0.98
172 – 361	70	0.77	0.68 – 0.70	31	0.88

Table 3. Atomic parameters with estimated standard deviation for the compound $Eu_2(C_3H_2O_4)_3.8H_2O$.

Atom	Group	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	B/Å^2
Eu(1)		−5(2)	1/4	1598(1)	3.3(1)
Eu(2)		2218(2)	3/4	1970(1)	2.8(1)
O(1)	$-COO^-$	−1720(16)	5119(29)	3257(9)	2.5(4)
O(2)	$-COO^-$	−765(16)	4223(27)	2412(10)	3.3(4)
O(3)	$-COO^-$	−443(18)	4686(30)	838(10)	3.4(5)
O(4)	$-COO^-$	833(15)	5746(29)	1466(8)	1.8(4)
O(5)	$-COO^-$	1587(18)	5717(29)	2818(10)	3.7(5)
O(6)	$-COO^-$	1565(23)	4849(38)	3829(13)	5.7(6)
O(W1)	H_2O	1405(23)	1/4	2394(15)	3.3(6)
O(W2)	H_2O	1593(31)	1/4	843(17)	4.8(8)
O(W3)	H_2O	−1966(30)	1/4	1343(17)	4.5(8)
O(W4)	H_2O	2737(26)	3/4	841(15)	2.8(6)
O(W5)	H_2O	3656(28)	3/4	2821(15)	4.0(7)
O(W6)	H_2O	2742(24)	5080(39)	5004(15)	6.8(8)
O(W7)	H_2O	213(141)	4310(178)	4961(94)	19.1(4.6)
C(1)		−903(49)	1/4	3371(27)	4.9(1.3)
C(2)		−1115(23)	4108(43)	2989(15)	2.6(6)
C(3)		32(35)	3/4	663(20)	2.4(9)
C(4)		202(19)	5916(37)	998(12)	1.4(5)
C(5)		836(51)	3/4	3629(28)	5.3(1.4)
C(6)		1405(28)	5886(48)	3409(17)	3.7(7)

Table 4. Observed and calculated structure factors for the compound $Eu_2(C_2H_2O_4)_3.8H_2O$. In each group the running index h, $|F_o|$, and $|F_c|$ are given.

K= 0 L= 0
4 230 240
6 131 124
8 129 131
10 85 90
12 62 55
14 89 94

K= 0 L= 1
2 90 92
3 190 178
4 187 171
5 188 178
6 90 85
8 74 76
9 100 105
10 86 91
12 74 72
14 54 44

K= 0 L= 2
1 144 137
2 76 76
3 112 115
4 49 104
5 110 108
7 61 64
8 54 54
10 49 47
14 58 54

K= 0 L= 3
1 186 221
2 57 45
3 302 277
4 135 120
5 269 259
6 132 119
8 69 54
9 200 208
10 58 68
13 84 89

K= 0 L= 4
0 162 157
1 201 205
2 237 223
3 99 109
4 97 81
5 159 139
6 137 146
7 43 43
8 56 48
10 60 60
12 68 56

K= 0 L= 5
1 45 53
2 72 69
3 75 79
4 155 118
5 146 137
7 137 131
8 48 55
9 135 162
11 71 70
13 64 71

K= 0 L= 6
0 210 200
1 221 214
2 30 27
3 200 180
4 202 195
5 61 60
6 75 84
8 111 106
10 85 111
12 63 54
14 42 48

K= 0 L= 7
1 41 51
3 129 139
6 115 114
7 117 120
8 110 126
10 61 56
11 113 113
12 68 57

K= 0 L= 8
0 117 124
1 34 45
2 95 109
3 151 157
4 145 143
8 54 45

K= 0 L= 9
1 129 132
3 179 176
4 115 123
5 95 97
6 120 124
7 133 127
8 81 92
9 55 59
10 67 71
12 51 42
13 45 39

K= 0 L= 10
0 55 55
1 156 139
2 285 308
6 105 110
10 54 52
12 77 90

K= 0 L= 11
2 50 55
4 83 82
5 86 85
6 129 133
8 60 57
10 56 50
11 53 43

K= 0 L= 12
0 111 110
1 134 141
2 191 215
3 82 87
4 84 78
6 98 110
8 59 48
12 60 61

K= 0 L= 13
1 140 155
2 54 52
3 125 154
7 129 141
11 101 98

K= 0 L= 14
0 59 58
1 93 103
3 76 68
5 86 77

K= 0 L= 15
1 74 79
3 135 160
7 138 135
11 78 74

K= 0 L= 16
0 62 56
1 79 90
2 138 159
3 59 53
6 98 100
7 63 56
8 82 55

K= 0 L= 17
1 49 46
5 69 59
8 54 59

K= 0 L= 18
2 109 112
6 118 110

K= 0 L= 19
1 61 53
3 95 82
5 92 72
6 62 57
7 50 48
8 65 52
9 48 48

K= 0 L= 20
0 103 98
1 49 62
4 89 67

K= 0 L= 21
3 77 69
6 53 50
7 62 58

K= 0 L= 22
0 82 77
1 62 57
6 36 27
8 43 46

K= 0 L= 23
1 52 43
5 53 56

K= 0 L= 24
1 46 47
3 47 38

K= 0 L= 25
1 43 37

K= 1 L= 0
2 184 151
4 42 39
6 183 170
8 156 146
10 73 77
12 55 39

K= 1 L= 1
3 116 89
5 107 92
6 201 193
8 68 69
10 56 62
12 94 83

K= 1 L= 2
1 172 168
2 109 106
3 185 172
4 101 87
5 132 109
6 141 127
7 215 197
8 135 121
10 57 58
11 112 99
12 56 47
15 44 43

K= 1 L= 3
0 98 101
1 107 160
2 134 137
3 223 196
4 66 67
5 150 129

K= 1 L= 4
1 127 124
2 50 40
3 302 283
4 44 45
6 35 35
7 240 253
11 149 135

K= 1 L= 5
0 144 151
1 134 135
2 194 176
3 194 177
4 210 207
5 108 108
6 171 170
7 48 37
8 95 115
10 84 90

K= 1 L= 6
1 100 93
2 116 101
3 50 53
4 87 83
5 156 155
7 84 79
8 55 57
9 115 132

K= 1 L= 7
0 30 32
1 81 92
2 260 255
3 129 131
4 45 54
5 132 126
6 106 125
8 72 70
10 61 52
12 55 58

K= 1 L= 8
1 158 180
2 33 41
3 146 139
4 89 93
5 193 197
6 72 77
7 80 84
8 89 77
9 142 141
10 90 85
12 50 45

K= 1 L= 9
0 315 262
2 123 116
4 181 200
5 35 38
8 54 58

K= 1 L= 10
1 77 74
3 78 87
4 90 98
5 58 53
6 95 94
7 77 81
8 80 74
9 98 86

K= 1 L= 11
0 253 288
1 74 84
3 62 62
4 196 200
6 58 65
8 92 90
10 70 66

K= 1 L= 12
1 88 98
2 51 43
4 78 89
5 120 127
6 56 63
8 59 60
9 99 89

K= 1 L= 13
0 125 134
1 117 128
3 92 98
4 53 55

K= 1 L= 14
1 153 151
5 151 171
9 124 128

K= 1 L= 15
0 56 60
1 97 115
2 39 39
3 82 94
4 81 90
6 48 45

K= 1 L= 16
1 56 55
5 65 62
9 73 66

K= 1 L= 17
0 121 137
1 52 56
4 139 161
8 80 58
10 49 54

K= 1 L= 18
3 65 67
6 58 55
7 67 61
8 63 61

K= 1 L= 19
0 85 87
2 61 55
6 68 76

K= 1 L= 20
3 61 68
3 56 68
5 63 65

K= 1 L= 21
6 51 45

K= 2 L= 0
4 361 330
6 70 64
8 158 173
10 118 125

K= 2 L= 1
1 100 124
2 82 57
3 49 114
4 94 81
5 176 150
6 153 138
7 101 103
8 99 106
9 67 65
10 62 71

K= 2 L= 2
0 217 264
1 148 155
2 81 69
3 110 103
4 224 222
5 73 57
8 80 84
10 52 41

K= 2 L= 3
1 226 253
2 70 67
3 76 46
4 98 86
5 357 334
6 73 67
7 52 55
8 89 95
9 155 167
10 49 48

K= 2 L= 4
0 98 93
1 95 106
2 107 117
3 166 172
4 159 140
5 97 93
6 67 59
7 73 68
8 64 55
10 65 67

K= 2 L= 5
1 154 157
2 85 62
3 28 23
4 77 61
5 170 158
7 72 70
9 96 116

K= 2 L= 6
0 214 179
1 168 165
2 236 208
3 132 129
4 235 213
5 127 124
6 82 71
8 88 83
10 76 80

K= 2 L= 7
1 73 79
2 50 51
3 221 221
4 150 146
5 52 58
6 83 85
7 188 148
8 71 57
10 61 51
10 73 51
11 121 81

K= 2 L= 8
0 228 216
1 180 160
2 110 111
3 46 50
4 161 154
6 64 54

K= 2 L= 9
1 117 127
2 85 92
3 176 176
4 86 93
5 128 140
6 124 118
7 93 91
8 82 78
9 71 66
10 78 62
11 65 70

K= 2 L= 10
2 235 247
5 80 66
6 141 165
8 67 67

K= 2 L= 11
4 54 45
6 74 78
8 106 109

K= 2 L= 12
1 89 94
2 162 172
3 74 78
5 64 65
6 110 122
8 91 78

K= 2 L= 13
1 55 57
2 43 38
3 128 149
7 178 184

K= 2 L= 14
1 87 87
3 96 107

K= 2 L= 15
1 53 55
3 86 93
7 131 125

K= 2 L= 16
1 66 77
2 110 111
3 75 86
6 82 76

K= 2 L= 17
2 50 51

K= 2 L= 18
2 142 161

K= 2 L= 19
1 76 71
3 71 70
5 58 44

K= 2 L= 20
0 75 76
4 56 56

K= 2 L= 21
1 60 67
3 58 46

K= 2 L= 22
0 72 79
4 73 71

K= 2 L= 23
5 45 52

K= 2 L= 24
1 48 55

K= 3 L= 0
2 134 114
4 163 150
6 186 150
8 111 124
10 66 75

K= 3 L= 1
1 54 60
2 261 279
3 155 126
6 211 233
8 85 67
12 87 91

K= 3 L= 2
1 158 183
2 77 63
3 189 201
4 112 94
5 76 58
6 147 141
7 149 143
8 70 83
11 106 116

K= 3 L= 3
0 127 149
1 134 156
2 37 26
3 194 164
4 61 60
5 49 37
6 45 51

K= 3 L= 4
1 105 97
2 67 41
3 259 272
6 51 53
7 151 168
11 117 124

K= 3 L= 5
0 261 256
1 191 199
2 220 216
3 112 96
4 118 128
5 82 74
6 82 73
8 68 74
10 78 85

K= 3 L= 6
1 140 138
2 96 87
3 58 54
4 40 39
5 143 146
6 86 89
7 72 74
9 85 87

K= 3 L= 7
1 126 128
2 208 205
3 75 75
5 65 69
6 83 78
7 63 54

K= 3 L= 8
1 185 179
2 58 51
3 92 106
4 55 44
5 142 137
6 87 87
8 76 83
9 93 90

K= 3 L= 9
0 226 246
2 100 90
4 133 135

K= 3 L= 10
1 66 57
2 53 54
3 62 63
4 62 57
6 73 76
7 59 68
8 94 102

K= 3 L= 11
0 235 254
1 75 89
6 107 129
7 64 58
8 91 95

K= 3 L= 12
1 50 50
2 52 44
5 85 89
6 76 75

K= 3 L= 13
0 97 94
1 104 113
4 62 69
5 66 69

K= 3 L= 14
1 89 98
5 163 170

K= 3 L= 15
1 99 109
3 58 63

K= 3 L= 17
0 171 180
4 122 113

K= 3 L= 18
3 78 79

K= 3 L= 19
0 83 81
2 64 62

K= 3 L= 20
3 65 56

K= 4 L= 0
2 74 68
4 285 248
6 107 93
8 99 96
10 75 68

K= 4 L= 1
1 83 102
2 34 32
3 69 61
6 100 89
5 131 113
6 74 72
8 108 103
9 79 75
10 69 70

K= 4 L= 2
0 121 139
1 93 102
2 55 48
3 128 119
4 139 110
8 53 49

K= 4 L= 3
1 138 147
2 45 35
3 82 87
5 206 188
6 102 89
8 77 65
9 133 138

K= 4 L= 4
2 65 63
3 107 99
4 50 49
5 87 75

K= 4 L= 5
1 62 62
3 156 142
4 44 38
7 168 168

K= 4 L= 6
0 75 77
1 85 86
2 114 98
3 120 111
4 121 116
5 60 65
6 115 113
8 89 81

K= 4 L= 7
3 157 145
6 76 85
7 107 107
8 76 73

K= 4 L= 8
0 146 141
1 57 54
3 70 74
4 113 116

K= 4 L= 9
1 106 104
3 135 152
4 71 81
5 80 82
6 70 68
7 100 98

K= 4 L= 10
1 67 72
2 209 221
6 105 128

K= 4 L= 11
2 71 54
4 67 62
6 68 66

K= 4 L= 12
0 64 53
1 77 81
2 114 135
3 63 74
6 79 93

K= 4 L= 13
0 83 81
1 79 85
3 110 109
7 145 142

K= 4 L= 14
1 62 57
3 68 76

K= 4 L= 15
3 110 98

K= 4 L= 16
2 123 111

K= 4 L= 18
2 111 100

K= 5 L= 0
2 82 78
6 144 112
8 97 94

K= 5 L= 1
1 49 59
2 101 236
3 28 30
5 69 51
6 134 119
8 57 47

K= 5 L= 2
1 88 105
2 60 54
3 142 125
4 72 59
5 88 69
6 96 72
7 132 128
8 75 81

K= 5 L= 3
0 86 92
1 105 118
2 65 63
3 107 99
4 50 49
5 87 75

K= 5 L= 4
1 62 62
3 156 142
4 44 38
7 168 168

K= 5 L= 5
0 75 77
1 85 86
2 114 98
3 120 111
4 121 116
5 60 65
6 115 113
8 89 81

K= 5 L= 6
1 45 39
4 62 66
5 123 102
7 54 55

K= 5 L= 7
0 41 41

Table 4. Continued.

1	66	60	9	75	95	K= 5 L= 11		K= 5 L= 15		4	100	77	5	177	158	K= 6 L= 4		K= 6 L= 10	
2	139	146				0	152	180	1	69	73	5	96	79				0	92	96	2	132	143
3	84	81	K= 5 L= 9			4	114	130				6	94	71	K= 6 L= 6			1	70	73			
5	66	84	0	145	152				K= 5 L= 17						1	70	66	3	79	88	K= 6 L= 14		
6	86	78	2	90	85	K= 5 L= 13			4	84	95	K= 6 L= 2			2	82	87	4	102	92	2	108	115
			4	98	116	0	88	95				0	152	147	3	95	74						
K= 5 L= 8						1	89	83	K= 6 L= 0			1	82	72	4	80	71	K= 6 L= 7					
1	90	89	K= 5 L= 10			3	75	75	4	134	135	4	56	60	5	76	70	3	95	85			
3	72	76	1	61	55																		
4	67	60	3	62	57	K= 5 L= 14		K= 6 L= 1				K= 6 L= 3			K= 6 L= 5			K= 6 L= 8					
5	114	128	4	77	67	1	104	104	1	70	84	1	102	133	5	115	85	0	92	85			
6	61	58				5	105	118	2	55	54	4	91	84									

These results of absorption correction are consistent with those found by Werner and Srivastava *et al.* and the correction applied was considered to be better than no correction at all. Thus the atomic parameters obtained from the corrected material are used to describe the structure.

The function minimized in the refinements was $\sum w(|F_o|-|F_c|)^2$ with weights according to Cruickshank.[8] In addition the two reflexions not obeying the condition $0.33 \leq |F_o|/|F_c| \leq 3.00$ were given zero weight. All observed reflexions were included in the calculation of R. The atomic scattering factors for the neutral atoms were taken from International Tables [3] for oxygen and carbon and from Cromer *et al.*[9] for europium.

The weighting scheme used was satisfactory as indicated by the approximate constancy of the averages of $w(|F_o|-|F_c|)^2$ between different $|F_o|$ and sin θ intervals (Table 2). The shifts in all parameters were less than 5 % of their estimated standard deviations in the last cycle of refinement.

The final atomic parameters with their estimated standard deviations are given in Table 3. The isotropic temperature factor of O(W7) at (0.02, 0.42, 0.50) is very large, 19 Å^2, indicating a high degree of disorder for this water molecule. This interpretation seems reasonable when regarding the surroundings of O(W7) as discussed below.

The electron density maps of a difference synthesis based upon the parameters given in Table 3 showed only spurious peaks $1-2$ e/Å^3 above a slightly varying background. The observed and calculated structure factors are compared in Table 4.

All computations were performed on the UNIVAC 1108 computer at Lund, Sweden, using the programs PIRUM,[10] DRF, DATAP2, LALS, DISTAN, PLANE, CELSIUS, and ORTEP.[11]

DESCRIPTION OF THE STRUCTURE

The superscripts (i) – (viii) are used to indicate the following equivalent positions of the structure

	x,y,z	(iii)	$x-1/2,1/2-z$	(vi)	$1/2+x,3/2-y,1/2-z$
(i)	$x,1/2-y,z$	(iv)	$x-1/2,y-1,1/2-z$	(vii)	$1/2-x,1-y,1/2+z$
(ii)	$x,3/2-y,z$	(v)	$1/2+x,y,1/2-z$	(viii)	$-x,1-y,1-z$

where x,y,z are the atomic coordinates given in Table 3. The numbering of the atoms constituting the three independent malonate ions, referred to as ligand 1, ligand 2, and ligand 3, is given in Fig. 4.

The structure consists of europium-malonate layers parallel with (001) and located around $z=1/4$ and $z=3/4$. The layer around $z=1/4$ is illustrated in Fig. 1 and may be described in the following way. Ligand 2 connects the

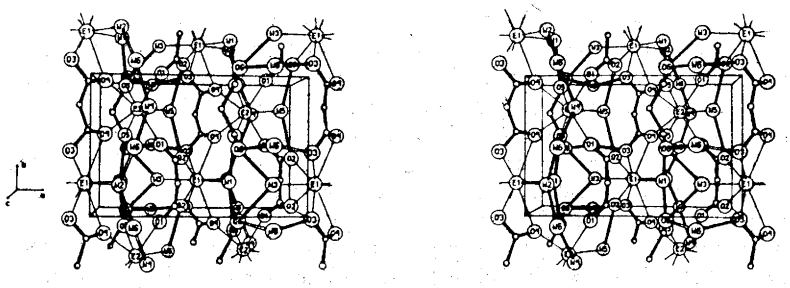

Fig. 1. A stereoscopic pair of drawings showing part of the europium malonate layer around $z=1/4$. The europium ions are denoted E1 and E2 and the water molecules W1, W2, *etc.* Bonds within the malonate ions are filled, hydrogen bonds are open, and Eu – O bonds are single lines. The box outlined is $-1/2\leq x\leq 1/2$, $0\leq y\leq 1$, $0\leq z\leq 1/2$.

europium ions by oxygen bridges Eu(1) – O(4) – Eu(2), in chains parallel with the b-axis. These chains are linked to layers by bridges of the type Eu(2) – O(1)C(2)O(2) – Eu(1) formed by ligand 1. Ligand 3 is not bridging. Each of the three malonate ions forms a six-membered chelate ring with europium.

There are seven non-equivalent water molecules in the structure. Five of them, O(W1) – O(W5), are coordinated to europium. O(W1), O(W3), and O(W5) are hydrogen bonded to carboxylate oxygens within the europium malonate layer, forming "water malonate" chains of the sequences – O(W1) – O(5) – CCC – O(5) – O(W1) –, – O(W3) – O(6) – CCC – O(6) – O(W3) –, and – O(W5) – O(2) – CCC – O(2) – O(W5) –, respectively. These chains run in the y-direction.

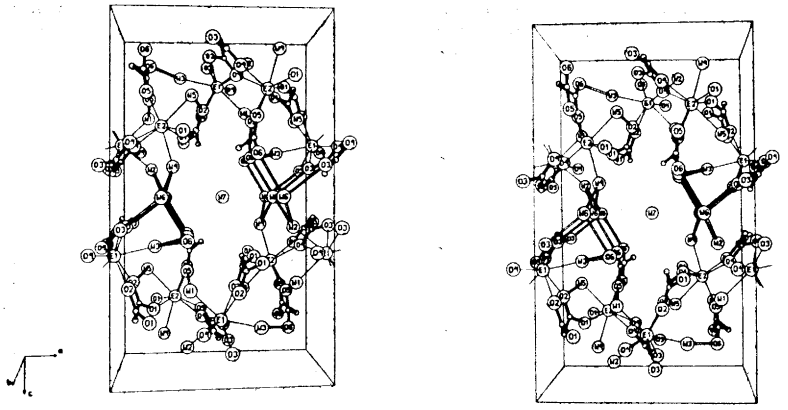

Fig. 2. A stereoscopic pair of drawings showing part of two adjacent europium malonate layers and the bonding between them. The atoms and bonds are indicated as in Fig. 1. The box outlined is $-1/2\leq x\leq 1/2$, $0\leq y\leq 1$, $0\leq z\leq 1$.

The water molecules O(W2) and O(W4) are bonded to the uncoordinated water molecule O(W6) forming a hydrogen bonded water chain of the sequence $-O(W2)-O(W6)-O(W4)-O(W6)-O(W2)-$. Also this chain runs in the y-direction.

The water molecule O(W6) is situated between the layers at $z \approx 0$ and $z \approx 1/2$, and adjacent layers are held together by hydrogen bonds *via* this water molecule, as illustrated in Fig. 2. The packing of the layers results in fairly wide oxygen bounded channels around $x = 0$, $z = 1/2$, and $x = 1/2$, $z = 0$. The disordered water molecule O(W7) is located in these channels.

The coordination polyhedra. The two crystallographically independent europium ions have different coordination numbers. Eu(1) is surrounded by nine oxygens forming a distorted tricapped trigonal prism (TCTP), while Eu(2) is surrounded by eight oxygens at the corners of a distorted square antiprism (SAP). The two polyhedra are illustrated in Fig. 3 and it is seen that they share the corner O(4). Their dimensions are given in Table 5 A and B.

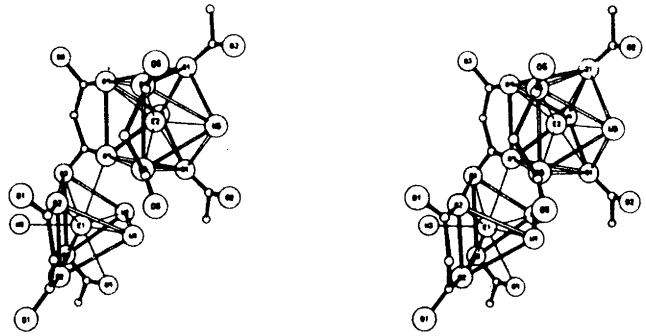

Fig. 3. A stereoscopic pair of drawings showing the coordination around the two europium ions. The notation of the atoms is as in Fig. 1. The edges of the square antiprism and the trigonal prism are open, bonds within the malonate ions are filled, and Eu – O bonds are single lines.

Table 5. Selected distances (Å) and angles (°) with their estimated standard deviations.

A. The coordination polyhedron around Eu(1)

Eu(1) – O(2)	2.37(2)	O(2) – O(W1)	3.00(3)
Eu(1) – O(3)	2.42(2)	O(2) – O(W3)	2.99(4)
Eu(1) – O(4)	2.84(2)	O(3) – O(3^{i})	3.54(5)
Eu(1) – O(W1)	2.38(3)	O(3) – O(4)	2.20(3)
Eu(1) – O(W2)	2.50(4)	O(3) – O(W2)	3.06(4)
Eu(1) – O(W3)	2.46(4)	O(3) – O(W3)	2.77(4)
O(2) – O(2^{i})	2.79(4)	O(4) – O(W1)	3.32(3)
O(2) – O(3)	3.28(3)	O(4) – O(W2)	3.07(3)
O(2) – O(4)	3.02(3)	O(W1) – O(W2)	3.19(5)

Table 5. Continued.

B. The coordination polyhedron around Eu(2)			
Eu(2) – O(1^{v})	2.37(2)	O(4) – O(4^{ii})	2.84(4)
Eu(2) – O(4)	2.44(2)	O(4) – O(5)	2.93(3)
Eu(2) – O(5)	2.39(2)	O(4) – O(W4)	3.02(3)
Eu(2) – O(W4)	2.41(3)	O(5) – O(5^{ii})	2.89(5)
Eu(2) – O(W5)	2.48(3)	O(5) – O(W5)	2.92(4)
O(1^{v}) – O(4)	3.09(3)	O(4) – Eu(2) – O(5^{ii})	116(1)
O(1^{v}) – O(5)	3.07(3)	O(W4) – Eu(2) – O(W5)	119(1)
O(1^{v}) – O(W4)	2.76(3)	O(1^{v}) – Eu(2) – O(1^{vi})	109(1)
C. Ligand 1			
C(1) – C(2)	1.54(5)	C(2) – C(1) – C(2^{i})	115(4)
C(2) – O(1)	1.23(4)	O(1) – C(2) – O(2)	125(3)
C(2) – O(2)	1.27(4)	O(1) – C(2) – C(1)	118(3)
O(2) – O(2^{i})	2.79(4)	O(2) – C(2) – C(1)	119(3)
Dihedral angles:	C(2^{i}) – C(1) – C(2) – O(1)		128
	C(2^{i}) – C(1) – C(2) – O(2)		45
D. Ligand 2			
C(3) – C(4)	1.47(4)	C(4) – C(3) – C(4^{ii})	122(3)
C(4) – O(3)	1.31(3)	O(3) – C(4) – O(4)	119(3)
C(4) – O(4)	1.24(3)	O(3) – C(4) – C(3)	117(2)
O(4) – O(4^{ii})	2.84(4)	O(4) – C(4) – C(3)	123(3)
	Dihedral angles	C(4^{ii}) – C(3) – C(4) – O(3)	146
		C(4^{ii}) – C(3) – C(4) – O(4)	28
E. Ligand 3			
C(5) – C(6)	1.55(5)	C(6) – C(5) – C(6^{ii})	115(5)
C(6) – O(5)	1.24(4)	O(5) – C(6) – O(6)	126(4)
C(6) – O(6)	1.22(5)	O(5) – C(6) – C(5)	117(4)
O(5) – (O(5^{ii})	2.89(5)	O(6) – C(6) – C(5)	117(3)
	Dihedral angles	C(6^{ii}) – C(5) – C(6) – O(5)	55
		C(6^{ii}) – C(5) – C(6) – O(6)	130
F. Possible hydrogen bonds			
O(W1) – O(5)	2.76(3)	O(W5) – O(2^{v})	2.79(2)
O(W2^{vii}) – O(W6)	2.74(4)	O(W6) – O(3^{v})	2.83(4)
O(W3) – O(6^{iii})	2.64(4)	O(W6) – O(6)	2.82(4)
O(W4^{vii}) – O(W6)	2.77(4)		
G. Distances shorter than 3.5 Å around O(W7)			
O(W7) – O(W6)	3.2(2)	O(W7) – O(W7^{i})	2.9(3)
O(W7) – O(6)	2.9(2)	O(W7) – O(W7^{viii})	1.2(3)
O(W7) – O(6^{viii})	3.4(2)	O(W7) – O(W4^{vii})	3.4(2)

The oxygens around Eu(1) are contributed by three malonate ions and three water molecules. The Eu(1)–O bond distances are in the range 2.37–2.84 Å. Their average value, 2.51 Å, is the same as found for ninecoordinated europium in europium trisglycolate.[12] The bond Eu(1)–O(4), 2.84 Å, is considerably longer than the average value. It is part of the oxygen bridge Eu(1)–O(4)–Eu(2) formed by the bridging-chelating carboxylate group –C(3)O(3)O(4). The distance Eu(2)–O(4) is not significantly different from the other Eu(2)–O bond distances. Similar asymmetric oxygen bridges are found in the malonates $Nd_2mal_3.nH_2O$, $n = 8$ and 6, and also in a number of other lanthanoid carboxylate structures.[1,2] The distance Eu(1)···Eu(2) is 4.20 Å and the next shortest Eu···Eu distance is Eu(2)···Eu(1^{v}), 6.05 Å.

The triangular faces of the TCTP – O(2)O(2^{i})O(W1) and O(3)O(3^{i})O(W2) – have the average edge length 3.08 Å. Two edges have lengths significantly different from this value *viz.* O(2)–O(2^{i}), 2.79 Å, and O(3)–O(3^{i}), 3.54 Å. O(2)–O(2^{i}) is the bite of ligand 1, and the oxygens O(3) and O(3^{i}) belong to bridging-chelating carboxylate groups of different malonate ions. The angle between the two triangular faces is 1° and the angles between each of these

Table 6. Deviations, in Å, from the least-squares planes within the coordination polyhedra and the malonate ions. The atoms defining the plane are in each case given above the asterisk.

A. The coordination polyhedra

Atom	Distance	Atom	Distance
O(1^{v})	0.08	O(2)	–0.10
O(1^{vi})	–0.02	O(W1)	0.10
O(W4)	–0.03	O(3)	0.10
O(W5)	–0.02	O(W2)	–0.10
*		*	

B. The carboxylate groups

Atom	Distance	Atom	Distance	Atom	Distance
C(1)	–0.01	C(3)	–0.01	C(5)	0.01
C(2)	0.04	C(4)	0.03	C(6)	–0.03
O(1)	–0.01	O(3)	–0.01	O(5)	0.01
O(2)	–0.01	O(4)	–0.01	O(6)	0.01
*		*		*	
Eu(1)	–0.47	Eu(1)	–0.15	Eu(2)	–1.01
Eu(2^{iii})	–0.43	Eu(2)	0.09		

C. The six-membered chelate rings

Atom	Distance	Atom	Distance	Atom	Distance
O(2)	0	O(4)	0	O(5)	0
C(2)	0	C(4)	0	C(6)	0
C(2^{i})	0	C(4^{ii})	0	C(6^{ii})	0
O(2^{i})	0	O(4^{ii})	0	O(5^{ii})	0
*		*		*	
C(1)	0.31	C(3)	0.67	C(5)	–0.45
Eu(1)	0.51	Eu(2)	0.29	Eu(2)	0.60

faces and the equatorial triangle, O(4)O(4^{i})O(W3), are 5° and 4°, respectively. The "rectangular" face O(2)O(2^{i})O(3)O(3^{i}) is planar for symmetry reasons and the other two "rectangular" faces are planar within 0.1 Å (Table 6A). Since O(3) and O(4) belong to the same carboxylate group the capping oxygen O(4) is restricted to a position far from equidistant from the four atoms of the capped face.

A regular TCTP is defined by the parameters ϱ and θ_{TP}.[13] ϱ is the ratio between the equatorial and prismatic metal-ligand bond lengths and θ_{TP} is the angle that the prismatic metal-ligand bonds make with the three fold axis. The average parameters of the present TCPT are $\varrho = 1.1$ and $\theta_{TP} = 48°$. The normal of the equatorial plane is taken as the three fold axis and the values of θ_{TP} range from 34° to 51°. The hard sphere value of θ_{TP} is 44° for $\varrho = 1.1$.

The oxygens coordinated to Eu(2) are contributed by four malonate ions and two water molecules. The Eu(2) – O bond distances are in the range 2.37 – 2.48 Å with the average 2.42 Å. This value is 0.05 Å less than that found in the eightcoordinated europium compound Eu(acetylacetonate)$_3$.3H$_2$O.[14] Variations of this magnitude in the average M – O bond distance are frequently found between different compounds of the same lanthanoid ion and coordination number (see Ref. 15, p. 37).

The two "square" faces of the SAP – O(4)O(4^{ii})O(5)O(5^{ii}) and O(1^{v})O(W4)O(1^{vi})O(W5) – are of about the same size. The average edge length is 2.87 Å with the maximum deviation 0.11 Å. The edges O(4)···O(4^{ii}) 2.84 Å, and O(5)···O(5^{ii}), 2.89 Å, are each spanned by a malonate ion forming a six-membered chelate ring with Eu(2). The corresponding square face is planar for symmetry reasons while the oxygens defining the other "square" face are coplanar within 0.1 Å (Table 6A). The angle between the two faces is 1°.

A regular SAP is defined by the angle, θ_{SAP}, that the metal-ligand bonds make with the eight fold inversion axis. The O-Eu(2) – O angles given in Table 5B represent $2\theta_{SAP}$. The average θ_{SAP} calculated from these angles is 57.5° as compared to the hard sphere value 59.3°.

Kepert[13] has shown that an increase in θ_{TP} and a decrease in θ_{SAP} both by 2 – 3° from the corresponding hard sphere value, minimize the ligand-ligand repulsive energy of a TCTP and a SAP, respectively. It is interesting to note that, even though the present polyhedra are irregular as a result of the geometrical constrains of the malonate ions and the interaction of the complexes with their crystallographic surroundings, the average values of θ_{TP} and θ_{SAP} are close to those predicted by Kepert's calculations.

There are three different six-membered europium-malonate chelate rings. In each ring the two C – O bonds are related by a mirror plane through the methylene carbon atom and the europium ion. Hence the four intra ring carboxylate atoms are coplanar. The rings formed by ligands No. 1 and 2 have a boat conformation with the europium ion and the methylene carbon atom at the same side of the OCCO-plane, while the ring formed by ligand 3 adopts a chair conformation with the europium ion and methylene carbon atom at opposite sides of the OCCO-plane (Table 6C). The boat conformation has invariably been found in previous X-ray structure analyses of malonate

complexes.[1,2,16] The chair conformation of the ring formed by ligand 3 is most probably determined by the possibilities of its uncoordinated oxygen, O(6), to be favourably hydrogen bonded.

The malonate ions. The dimensions of the malonate ions are given in Table 5C–E, and are also indicated in Fig. 4. They are in accordance with those found in other malonate structures.[1]

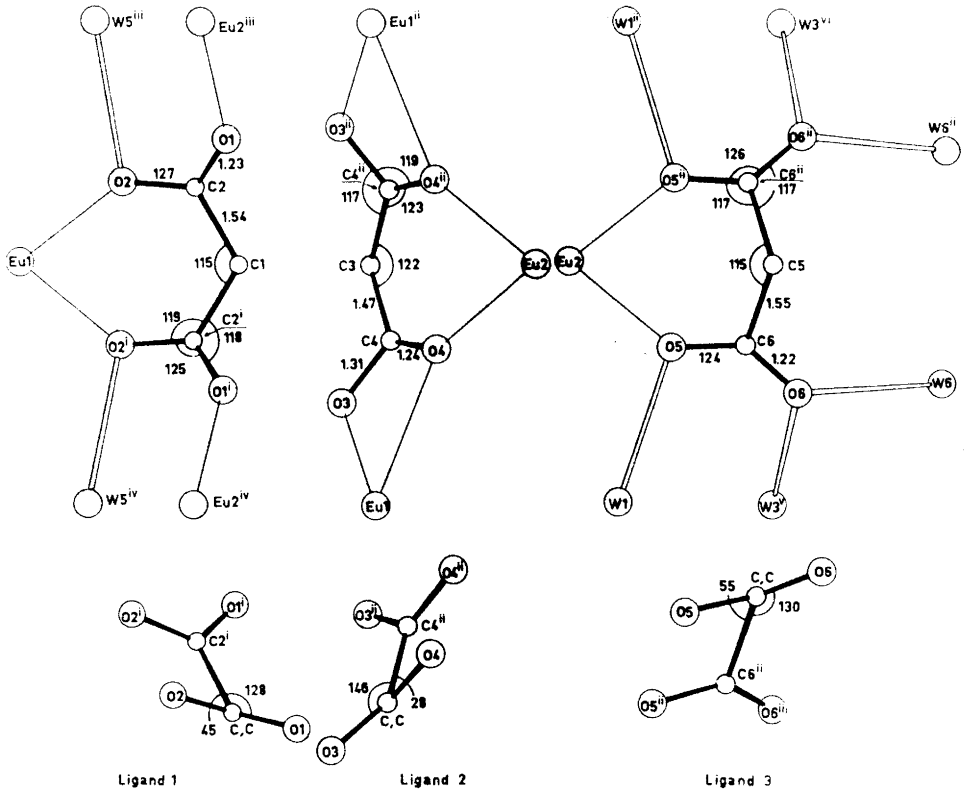

Fig. 4. The three malonate ions and their immediate surroundings, together with projections of each malonate ion along one of its C–C bonds. The angles indicated in these projections] are the dihedral angles C–C–C–O given in Table 5C, D, and E. The notation of the atoms and bonds is the same as in Fig. 1.

The three independent C–COO– groups are planar within the limits of errors (Table 6B). In each malonate ion the carboxylate groups are related by a mirror plane through the methylene carbon. The dihedral angles included in Table 5C–E and in Fig. 4 indicate that the two carboxylate groups are twisted in the same direction out of the carbon chain plane by about 30°, 50°, and 30° for ligands No. 1, 2, and 3, respectively. The corresponding ligand bites are 2.79 Å, 2.85 Å, and 2.89 Å.

The conformations of these malonate ions are similar to those found for the chelating malonate ions in $Nd_2mal_3.8H_2O$ [1] and $Nd_2mal_3.6H_2O$,[2] which have twist angles of about 40° and 45° and bites 2.80 Å and 2.83 Å.

The water molecules. The possible hydrogen bond distances around the water molecules O(W1) – O(W6) are given in Table 5F. They are selected by the criteria described before.[1]

The coordinated water molecules are situated in the mirror planes each forming two equivalent hydrogen bonds (see Fig. 1). Their donor angles, O···O(W)···O, are in the range 92 – 144° *i.e.* within the limits 60 – 150° found in other crystal hydrates.[17] The sum of the three bond angles around the water oxygen is 330° for O(W5), 344° for O(W4), and 350 – 360° for O(W1), O(W2), and O(W3).

The uncoordinated water molecule O(W6) is surrounded by four oxygens in an approximately tetrahedral arrangement *viz.* O(6) and O(3^{v}) which belong to one europium malonate layer and O($W4^{vii}$) and O($W2^{vii}$) which are coordinated to europium in an adjacent layer (see Fig. 2). Thus the hydrogen bonds of O(W6) link the layers together. The "tetrahedral" angles are in the range 83 – 138° and the donor angle O(6)···O(W6)···O(3^{v}) is 83°.

The water molecule O(W7) is situated in the channels running parallel with *b*. The channel centered at $x = 0$, $z = 1/2$ is illustrated in Fig. 2. It is bounded by oxygens at the levels $y = 0$ and $y = 1/2$ and by oxygen and methylene carbons at the levels $y = 1/4$ and $y = 3/4$, [*e.g.* O(1), O(6), O(W6), O(1^{viii}), O(6^{viii}) and O($W6^{viii}$) at $y = 1/2$ and O($W4^{vii}$), C(5^{viii}), and C(1) at $y = 1/4$]. Geometrically, any one of the bounding oxygens may act as an acceptor for a hydrogen bond from a water molecule in the channel. Regarding this fact, the fairly high temperature factor of O(W7) at (0.02, 0.43, 0.50) is interpreted as follows. The water molecules in the channel are distributed among a number of favourable positions around $x = 0$, $z = 1/2$, with a certain preference for the position (0.02, 0.43, 0.50). The latter position is surrounded by five oxygens at distances less than 3.4 Å (see Table 5G).

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