Possibly the energy required to deform even slightly the five-membered chelate ring in **3** upon formation of its anionic intermediate is responsible inasmuch as the ester oxygens in Cu(Etala-sal)$_2$ are coordinated weakly or not at all.[16]

Acknowledgment.—This research was supported by the National Institutes of Health under Grant GM-15471. We thank Dr. E. H. Abbott for a preprint of ref 22 and Dr. D. A. Buckingham for a copy of the thesis cited in footnote 36.

CONTRIBUTION FROM THE MATERIALS SCIENCE LABORATORIES, DEPARTMENT OF CHEMICAL ENGINEERING,
UNIVERSITY OF TEXAS AT AUSTIN, AUSTIN, TEXAS 78712, AND THE REACTOR CHEMISTRY DIVISION,
OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE 37830

The Crystal Structure of Erbium Oxalate Trihydrate[1]

BY H. STEINFINK AND G. D. BRUNTON

Received May 26, 1969

The compound $Er(C_2O_4)(HC_2O_4)\cdot 3H_2O$ crystallizes in space group P4/n with $a_0 = 8.6664$ (3) Å and $c_0 = 6.4209$ (8) Å at 24°. The measured density is 2.8 (1) g/cm^3 and the calculated density is 2.742 g/cm^3 so that there are two formula weights in the unit cell. Molybdenum radiation was used to measure the integrated intensities of 1641 independent reflections with a scintillation counter and a four-circle diffractometer. The parameters were refined by least squares to $R = 0.072$ using anisotropic temperature factors for all atoms except for the water molecules. The erbium atom is coordinated to eight oxygen atoms at distances of 2.362 (5)–2.418 (5) Å and they form a distorted square antiprism around the cation. A water molecule forms the ninth near neighbor at 2.441 (9) Å above the larger square face of the antiprism. The acid oxalate and oxalate anions occupy crystallographic sites at random. The "statistically averaged" oxalate group is centrosymmetric and planar with C—C = 1.529 (11) Å, C—O equivalent to C=O equals 1.254 (7) Å; the values of the angles are O(1)–C–O(2) = 125.9 (5)°, O(1)–C–C = 116.8 (7)°, and O(2)–C–C = 117.3 (6)°. Hydrogen bonding exists between $H_2O(1)$ and the oxygen atoms of the acid groups at distances of 2.73 (7) Å. A very short hydrogen bond, 2.43 (4) Å, is observed between two $H_2O(2)$ molecules but the physical significance is difficult to assess because $H_2O(2)$ is disordered in this structure. This compound occurs also for dysprosium, ytterbium, and yttrium analogs but could not be prepared for neodymium.

Introduction

The rare earth oxalate hydrates $Ln_2(C_2O_4)_3\cdot 10H_2O$ (Ln = La, Nd, Gd) have been prepared and characterized optically[2] and by X-ray diffraction powder data[2,3] which show that they are isomorphous. Some of the transuranic elements also form these oxalate hydrates and are isomorphous with the rare earth compounds.[3] No comparable oxalate hydrates for the heavy rare earth elements have been reported. Dr. R. H. Karraker of Eastern Illinois University undertook the preparation of oxalates of the heavy rare earths. It was observed that the powder X-ray diffraction diagrams of his oxalate preparations were different from the previously reported patterns for the lanthanide oxalate decahydrates and an analysis of the erbium compound indicated that the material has the formula $Er(HC_2O_4)(C_2O_4)\cdot 3H_2O$. The complete crystal structure analysis of this compound was undertaken because no structural investigation of a rare earth oxalate has been reported and because these materials contain both the acid monoanion and the dianion in the same structure. The presence of a dicarboxylic acid molecule together with its doubly charged ion has recently been reported for potassium hydrogen malonate.[4,5] Oxalic acid has different bond lengths for C=O and C—OH[6-8] and we planned to identify the bonding that exists between the cation and the two different anions. Also, the oxalate ion is not always planar[9] and the conformation of the oxalate ion in this compound is therfore also of interest.

Experimental Section

Erbium oxalate trihydrate, $Er(HC_2O_4)(C_2O_4)\cdot 3H_2O$, was prepared by precipitating erbrium oxalate from an aqueous solution of erbium chloride and oxalic acid. The erbium oxalate precipitate was redissolved in concentrated HCl and pink crystals were grown by evaporating the HCl slowly at room temperature. After about 1 week good crystals were obtained. A similar technique was used to prepare the Dy, Yb, and Y analogs of the erbium compound but the Nd isomorph could not be prepared. Results of a wet chemical analysis of the crystals follow (as weight per cent). *Anal.* Calcd for $Er(HC_2O_4)(C_2O_4)\cdot 3H_2O$: Er, 41.99; oxalate, 44.45; H_2O, 13.56. Found: Er, 40.8; oxalate, 43.6; H_2O, 15.4.

Precession photographs of a crystal show the diffraction symmetry 4/m and the only observed systematic absences were $hk0$ with $h + k = 2n + 1$. These absences are characteristic solely of space group P4/n (C_{4h}, no. 85).

Most of the crystals are bounded by the forms {110} and {001}. A crystal bounded by these forms and with dimensions 0.312 × 0.390 × 0.299 ± 0.005 mm was mounted on a Picker four-circle automatic single-crystal diffractometer. The takeoff angle was reduced to 1.2° and 32 reflection maxima between

---

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) V. Gilpin and W. G. McCrone, *Anal. Chem.*, **24**, 225 (1952).

(3) I. L. Jenkins, F. H. Moore, and M. J. Waterman, *J. Inorg. Nucl. Chem.*, **27**, 77 (1965).

(4) R. Parthasarathy, *Science*, **161**, 179 (1968).

(5) R. Parthasarathy, J. G. Sime, and J. C. Speakman, *Acta Crystallogr., Sect. B*, **25**, 1201 (1969).

(6) E. G. Cox, M. W Dougill, and G. A. Jeffrey, *J. Chem. Soc.*, 4854 (1952).

(7) G. E. Ahmed and D. W. J. Cruickshank, *Acta Crystallogr.*, **6**, 385 (1953).

(8) R. G. Delaplane and J. A. Ibers, *J. Chem. Phys.*, **45**, 3451 (1966).

(9) G. A. Jeffrey and G. S. Parry, *J. Chem. Soc.*, 4864 (1952).

TABLE I

ATOMIC PARAMETERS FOR $HEr(C_2O_4)_2 \cdot 3H_2O$

(PARAMETERS $\times 10^4$)

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Er	2500	2500	747.0 (6)[b]	13.7 (4)	13.7 (4)	112 (1)	0	0	0
O(1)	1297 (6)	255 (6)	2056 (8)	55 (5)	49 (5)	148 (9)	−27 (5)	−37 (6)	23 (6)
O(2)	461 (6)	1602 (5)	8482 (8)	41 (5)	32 (4)	159 (10)	−14 (4)	−17 (6)	20 (5)
C	5391 (7)	239 (7)	1017 (8)	31 (5)	29 (5)	133 (10)	8 (5)	−7 (6)	−12 (6)
$H_2O(1)$	2500	2500	4548 (14)	65 (5)	c	c	c	c	c
$H_2O(2)$	1199 (21)	6984 (21)	4425 (17)	99 (8)	c	c	c	c	c

[a] Coefficients in the temperature factor: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}kl + 2\beta_{23}kl)]$. [b] The number in parentheses is the standard error in terms of the last significant digit, as derived from the variance–covariance matrix. [c] Temperature factors constrained to be isotropic.

47 and 60° 2θ were centered automatically for Mo $K\alpha_1$ (λ 0.70926 Å).[10] These precise 2θ measurements were used in a least-squares refinement for the lattice constants yielding $a_0 = 8.6664 \pm 0.0003$ and $c_0 = 6.4209 \pm 0.0008$ Å at 24°. The densities of several crystals were measured with a Berman balance and averaged 2.8 (1) g/cm^3. The calculated density is 2.742 g/cm^3 on the assumption of two formula weights per unit cell.

The diffraction intensities were collected from independent spectra occurring between 10 and 80° 2θ with unfiltered Mo $K\alpha$ radiation and a scintillation-counter detector. An angular range of 1.6° was step scanned in increments of 0.01° with 0.5-sec counts at each step and the background was measured on each side of the peak for 20 sec.[10] The data were corrected for Lorentz, polarization, and absorption effects (μ = 90.93 cm^{-1}). The transmission factor varied from 0.082 to 0.217. A standard reflection (666) was measured after every 20 reflections throughout the collection of intensity data to check on intensity drift. One measurement of the standard reflection was assigned unit value and all others were expressed as fractions of this value. The intensity measurements obtained between two successive measurements of the standard reflection were multiplied by the appropriate ratio so that all intensities were referred to a single value of the (666) intensity. The ratios varied from 3.34 to 6.95.

Structure Determination

The presence of two formula units in the unit cell and the space group symmetry imposed limitations on the placement of the atoms. The molecular centers of the bioxalate and oxalate ions, if they are crystallographically distinguishable, must be placed in space group P4/n either in positions 2(a) or 2(b) which have a $\bar{4}$ point symmetry, or into 2(c) which has point symmetry 4. Symmetry $\bar{4}$ can be postulated for C_2O_4 provided the C═O and C—O distances are assumed equal, although the resultant dihedral angle of 90° between the two carboxyl groups is not probable; a 28° angle has been found in $(NH_4)_2C_2O_4 \cdot H_2O$.[7] It is not possible to have the $HC_2O_4^-$ ion conform to a $\bar{4}$ configuration if the unequal distances for C—OH and C═O are maintained. On the basis of these considerations the most likely structure will be one in which $C_2O_4^{2-}$ and $HC_2O_4^-$ ions randomly occupy crystallographic sites 4(d) with symmetry $\bar{1}$. The resulting structure confirms this initial hypothesis.

The position of the erbium ion was determined by interpretation of a three-dimensional Patterson function. The positions of the carbon and oxygen atoms and water molecules were deduced from successive three-dimensional F_o and $F_o - F_c$ electron density maps. The structural parameters were refined by a modification of the Busing, Martin, and Levy ORFLS computer program.[11] The quantity refined by the least-squares program was $\Sigma w(sF_o^2 - F_c^2)^2$ with weights, w, equal to the reciprocals of the variances which were estimated from the empirical equation

$$\sigma^2(F_o^2) = [T + B + (0.05(T - B))^2]/[A(Lp)^2]$$

where T is the total counts, B is the background counts, A is the absorption correction, and Lp is Lorentz and polarization factors. The scattering factors for the neutral atoms were taken from Cromer and Waber.[12] The Er scattering was corrected for the real ($\Delta f'$) and imaginary contributions ($\Delta f''$) of anomalous dispersion.[13] Anisotropic temperature factors were calculated for all of the atoms except for the water molecules which were constrained to be isotropic. The multiplicity of $H_2O(2)$ was varied as a least-squares parameter but the final result (0.42 ± 0.04) is within 3σ of the theoretical value of 0.5. Therefore, the theoretical value was used for the final refinement. The final atomic parameters and temperature factors are listed in Table I. A three-dimensional difference Fourier map was calculated with this last set of parameters and no physically significant electron density peaks were observed.

The discrepancy indices are

$$R_1 = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2 = 0.147$$

$$R_2 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.072$$

$$R_3 = (\Sigma w(F_o^2 - F_c^2)^2)^{1/2}/(\Sigma(F_o^2)^2)^{1/2} = 0.161$$

for 1641 independent reflections, Table II. The final values of F_c are corrected for extinction[14] ($r^* = -0.014$ (2) Å). The standard deviation of a reflection of unit weight $[\Sigma w(F_o - F_c)^2/(n_o - n_v)]^{1/2}$ is 2.56 (n_o = number of observations and n_v = number of variables).

Discussion

The erbium ion is coordinated to eight oxygen ions which form a distorted square antiprism and to $H_2O(1)$. A square 3.12 (1) Å on edge consisting of four O(1) atoms exists on one side of Er and four O(2) atoms

---

[10] W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and R. T. Roseberry, USAEC Report ORNL-4143, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1968.

[11] W. R. Busing, K. O. Martin, and H. A. Levy, USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1952.

[12] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

[13] C. H. Dauben and D. H. Templeton, *ibid.*, **8**, 841 (1955).

[14] W. H. Zachariasen, *ibid.*, **23**, 558 (1967).

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10) FOR $Er(C_2O_4)(HC_2O_4) \cdot 3H_2O$[a]

L	FOBS	FCAL
	0 0 L	
2	363	495
3	561	-693
4	364	-430
5	367	-397
6	460	-508
7	421	-405
8	340	-310
9	57	-59
10	0	7
11	129	75
	0 1 L	
2	622	-748
3	684	-882
4	620	-740
5	564	-635
6	224	-237
7	62	42
8	292	252
9	287	243
10	233	183
11	138	105
	0 2 L	
1	461	-498
2	930	-967
3	268	-308
4	94	113
5	416	439
6	466	493
7	379	363
8	312	292
9	147	137
10	63	48
11	87	-56
	0 3 L	
1	456	447
2	965	993
3	1001	1098
4	727	814
5	331	361
6	64	75
7	73	-49
8	167	-145
9	214	-182
10	246	-197
11	167	-130
	0 4 L	
0	1444	1339
1	1024	1064
2	701	700
3	122	123
4	265	-281
5	489	-533
6	471	-520
7	390	-398
8	228	-236
9	95	-81
10	35	10
11	103	70
	0 5 L	
1	426	-422
2	680	-686
3	801	-804
4	635	-653
5	413	-449
6	132	-141
7	60	43
8	188	179
9	219	189
10	201	172
11	151	115
	0 6 L	
0	851	-713
1	597	-615
2	585	-604
3	230	-245
4	109	105
5	395	399
6	429	459
7	351	363
8	236	238
9	110	101
10	56	20
	0 7 L	
1	497	501
2	666	691
3	784	813
4	490	489
5	332	339
6	54	52
7	0	-28
8	135	-134
9	164	-153
10	176	-152
	0 8 L	
0	974	828
1	612	612
2	375	388
3	65	75
4	106	-100
5	293	-286
6	372	-392
7	345	-358
8	249	-235
9	88	-69
10	38	13
	0 9 L	
1	394	-386
2	465	-499
3	522	-554
4	398	-417
5	380	-389
6	148	-157
7	56	23
8	196	189
9	215	194
	0 10 L	
0	889	-786
1	630	-636
2	290	-313
3	27	23
4	210	206
5	296	296
6	283	295
7	251	263
8	179	188
	0 11 L	
1	144	145
2	311	329
3	449	505
4	426	458
5	279	299
6	76	79
7	48	-35
8	123	-114
	0 12 L	
0	453	433
1	408	411
2	281	309
3	100	101
4	109	-114
5	232	-244
6	237	-249
7	198	-211
	0 13 L	
1	237	-232
2	351	-376
3	381	-428
4	306	-348
5	211	-236
6	73	-75
	0 14 L	
0	495	-498
1	401	-406
2	230	-247
3	36	-34
4	119	128
5	216	241
	0 15 L	
1	128	145
2	216	245
3	277	308
	1 0 L	
2	605	-748
3	692	-882
4	619	-740
5	568	-635
6	233	-237
7	71	42
8	290	252
9	278	243
10	232	183
11	145	105
	1 1 L	
2	551	-578
3	59	-47
4	234	256
5	430	464
6	465	471
7	431	421
8	290	267
9	137	120
10	25	11
11	80	-59
	1 2 L	
1	961	971
2	1235	1287
3	1074	1180
4	613	674
5	357	415
6	85	88
7	82	-49
8	200	-189
9	237	-203
10	224	-185
11	159	-121
	1 3 L	
0	1385	1257
1	657	665
2	740	740
3	239	244
4	42	-30
5	357	-390
6	523	-582
7	462	-486
8	317	-307
9	84	-66
10	55	24
11	104	76
	1 4 L	
1	770	-756
2	850	-846
3	785	-777
4	438	-432
5	390	-412
6	165	-181
7	49	-49
8	160	146
9	211	192
10	216	180
11	161	125
	1 5 L	
0	1343	-1195
1	743	-716
2	694	-714
3	92	-76
4	248	233
5	430	442
6	439	458
7	301	322
8	253	254
9	99	99
10	39	27
11	91	-63
	1 6 L	
1	223	208
2	615	628
3	949	979
4	819	832
5	408	414
6	25	27
7	135	-129
8	200	-197
9	190	-179
10	193	-157
	1 7 L	
0	911	775
1	649	626
2	526	556
3	154	146
4	185	-176
5	394	-389
6	396	-402
7	297	-306
8	234	-224
9	121	-105
10	43	-24
	1 8 L	
1	337	-314
2	479	-499
3	469	-483
4	462	-467
5	358	-353
6	193	-191
7	46	-9
8	139	134
9	175	161
	1 9 L	
0	1042	-900
1	679	-651
2	303	-321
3	53	27
4	181	169
5	297	291
6	335	349
7	298	301
8	191	195
9	54	66
	1 10 L	
1	270	257
2	428	450
3	529	562
4	485	512
5	349	362
6	99	109
7	89	-80
8	199	-191
	1 11 L	
0	703	614
1	487	480
2	313	326
3	0	39
4	123	-144
5	244	-252
6	264	-273
7	223	-232
8	180	-184
	1 12 L	
1	259	-251
2	362	-380
3	339	-421
4	279	-313
5	225	-235
6	88	-104
7	24	-18
	1 13 L	
0	483	-453
1	386	-382
2	261	-279
3	79	-86
4	71	86
5	213	230
6	259	284
	1 14 L	
1	207	208
2	326	345
3	370	303
4	281	312
5	168	191
	1 15 L	
0	322	341
1	306	319
2	238	244
3	85	85
	2 0 L	
1	466	-498
2	916	-967
3	270	-308
5	414	439
6	469	483
7	379	363
8	314	292
9	162	137
10	64	48
11	76	-56
	2 1 L	
1	224	225
2	500	493
3	1095	1254
4	694	775
5	467	549
6	52	46
7	53	-30
8	171	-155
9	205	-178
10	225	-187
11	191	-140
	2 2 L	
0	1620	1747
1	1046	1095
2	839	838
3	171	173
4	225	-242
5	510	-562
6	533	-592
7	422	-437
8	253	-254
9	63	-67
10	50	18
11	82	77
	2 3 L	
1	1194	-1199
2	1190	-1206
3	918	-909
4	433	-432
5	399	-435
6	143	-163
7	21	12
8	206	208
9	238	215
10	103	170
11	141	110
	2 4 L	
0	1308	-1096
1	907	-905
2	326	-330
3	94	-96
4	59	51
5	271	278
6	393	426
7	427	452
8	279	283
9	125	107
10	41	-6
11	67	-51
	2 5 L	
1	290	285
2	522	529
3	773	796
4	681	674
5	481	499
6	151	151
7	33	-41
8	196	-195
9	226	-206
10	203	-172
	2 6 L	
0	1288	1072
1	919	934
2	512	513
3	54	-17
4	341	-352
5	449	-452
6	342	-350
7	265	-274
8	190	-206
9	133	-127
10	42	-28
	2 7 L	
1	289	-271
2	466	-470
3	682	-726
4	559	-575
5	431	-434
6	91	-108
7	61	40
8	178	174
9	190	186
10	181	159
	2 8 L	
0	966	-810
1	619	-615
2	417	-437
3	89	-81
4	156	151
5	330	337
6	382	392
7	310	320
8	210	216
9	71	80
	2 9 L	
1	299	295
2	443	469
3	564	608
4	451	471
5	335	338
6	75	85
7	42	-34
8	134	-134
9	151	-149
	2 10 L	
0	662	557
1	487	469
2	375	386
3	104	113
4	124	-128
5	288	-298
6	313	-318
7	229	-239
8	164	-165
	2 11 L	
1	276	-266
2	426	-432
3	437	-475
4	379	-397
5	257	-271
6	107	-100
7	33	33
8	133	130
	2 12 L	
0	660	-589
1	498	-468
2	256	-271
3	82	-49
4	96	98
5	219	236
6	293	317
7	282	292
	2 13 L	
1	296	281
2	404	415
3	357	385
4	259	289
5	173	189
6	87	88
	2 14 L	
0	324	331
1	286	295
2	243	251
3	93	101
4	49	-55
5	161	-178
	2 15 L	
1	132	-140
2	262	-275
3	328	-361
	3 0 L	
1	487	447
2	1012	993
3	1026	1088
4	733	814
5	333	361
6	83	75
7	69	-49
8	162	-145
9	212	-182
10	237	-197
11	180	-130
	3 1 L	
0	1312	1154
1	985	966
2	1013	982
3	223	200
4	337	-367
5	561	-613
6	457	-490
7	312	-313
8	231	-229
9	138	-124
10	60	-38
11	93	64
	3 2 L	
1	173	-152
2	597	-576
3	807	-780
4	823	-844
5	481	-500
6	177	-183
7	46	55
8	186	193
9	214	195
10	216	182
11	151	117
	3 3 L	
0	1716	-1491
1	839	-789
2	580	-554
3	0	-18
4	147	142
5	348	347
6	417	457
7	369	384
8	279	280
9	122	97
10	55	18
11	79	-55
	3 4 L	
1	598	574
2	855	837
3	925	916
4	628	673
5	455	461
6	113	114
7	83	-83
8	226	-223
9	220	-210
10	191	-166
11	126	-100
	3 5 L	
0	1539	1316
1	844	795
2	609	610
3	0	-19
4	270	-268
5	445	-433
6	432	-445
7	305	-314
8	237	-236
9	101	-84
10	37	-20
	3 6 L	
1	273	-241
2	390	-378
3	578	-576
4	531	-528
5	502	-497
6	217	-211
7	28	-14
8	164	172
9	217	197
10	187	163
	3 7 L	
0	1177	-990
1	748	-695
2	331	-341
3	90	28
4	151	147
5	270	263
6	333	343
7	328	335
8	245	245
9	108	93
10	39	4
	3 8 L	
1	514	481
2	692	720
3	677	710
4	478	489
5	282	286
6	81	68
7	73	-59
8	155	-162
9	181	-173
	3 9 L	
0	579	467
1	550	506
2	460	473
3	217	226
4	118	-124
5	372	-374
6	373	-390
7	294	-300
8	167	-179
9	90	-78
	3 10 L	
1	209	-197
2	376	-380
3	478	-516
4	394	-417
5	260	-262
6	85	-74
7	33	-8
8	72	73
	3 11 L	
0	641	-554
1	492	-468
2	313	-302
3	72	-71
4	87	115
5	235	255
6	274	295
7	240	254
8	162	163
	3 12 L	
1	313	294
2	413	420
3	434	458
4	322	349
5	240	263
6	76	75
7	58	-54
	3 13 L	
0	468	457
1	377	376
2	253	248
3	42	67
4	91	-77
5	179	-202
6	239	-259
	3 14 L	
1	159	-163
2	278	-284
3	334	-361
4	285	-307
	3 15 L	
0	379	-420
1	339	-349
2	185	-199
	4 0 L	
0	1441	1321
1	1108	1063
2	749	700
3	138	123
4	269	-281
5	491	-533
6	470	-520
7	391	-398
8	234	-236
9	102	-81
10	44	10
11	89	70
	4 1 L	
1	438	-411
2	604	-563
3	1052	-1061
4	702	-722
5	569	-619
6	107	-108
7	69	76
8	260	252
9	249	234
10	208	175
11	133	104
	4 2 L	
0	1781	-1634
1	987	-950
2	465	-452
3	144	137
4	269	256
5	314	326
6	335	347
7	302	320
8	283	274
9	151	140
10	58	46
11	54	-47
	4 3 L	
1	297	277
2	496	476
3	856	839
4	682	647
5	512	515
6	137	134
7	29	-24
8	176	-177
9	209	-192
10	195	-171
11	141	-114
	4 4 L	
0	1024	803
1	812	772
2	726	728
3	262	235
4	258	-250
5	521	-532
6	489	-486
7	317	-335
8	208	-208
9	101	-93
10	48	-10
	4 5 L	
1	398	-341
2	669	-679
3	793	-802
4	657	-656
5	371	-357
6	81	-77
7	64	62
8	147	147
9	160	164
10	192	168
	4 6 L	
0	1131	-921
1	744	-690
2	393	-400
3	86	-67
4	126	123
5	324	316
6	393	405
7	355	360
8	225	229
9	91	91
10	20	4
	4 7 L	
1	518	485
2	633	649
3	541	561
4	440	445
5	360	358
6	182	176
7	0	-25
8	187	-191
9	186	-198
	4 8 L	
0	860	687
1	552	498
2	408	409
3	114	112
4	70	-80
5	273	-273
6	363	-375
7	319	-324
8	228	-227
9	83	-70
	4 9 L	
1	340	-311
2	519	-521
3	502	-593
4	395	-421
5	242	-238
6	50	-56
7	52	15
8	76	92
9	121	131
	4 10 L	
0	735	-618
1	534	-489
2	395	-392
3	81	-82
4	148	153
5	299	312
6	329	341
7	250	263
8	171	185
	4 11 L	
1	249	230
2	379	387
3	446	456
4	379	403
5	280	283
6	94	106
7	58	-37
	4 12 L	
0	521	502
1	420	402
2	241	241
3	65	31
4	111	-104
5	177	-190
6	194	-216
	4 13 L	
1	138	-129
2	259	-274
3	358	-384
4	352	-369
5	227	-240
	4 14 L	
0	415	-451
1	381	-389
2	253	-252
3	42	-43
4	117	137
	4 15 L	
1	171	181
	5 0 L	
1	459	-422
2	745	-686
3	859	-804
4	656	-653
5	428	-440
6	139	-141
7	55	43
8	191	179
9	215	189
10	197	172
11	146	115
	5 1 L	
0	1654	-1427
1	986	-913
2	402	-358
3	77	71
4	177	156
5	233	293
6	375	402
7	373	339
8	266	264
9	121	93
10	40	12
11	93	-46
	5 2 L	
1	596	540
2	777	740
3	737	698
4	646	609
5	492	496
6	227	225
7	60	-52
8	247	-247
9	261	-239
10	200	-164
	5 3 L	
0	1362	1098
1	964	917
2	577	532
3	91	67
4	278	-264
5	475	-441
6	429	-437
7	367	-362
8	238	-239
9	112	-99
10	13	6
	5 4 L	
1	357	-315
2	618	-590
3	857	-849
4	602	-568
5	355	-329
6	49	-43
7	0	9
8	83	89
9	135	140
10	205	175
	5 5 L	
0	587	-436
1	542	-477
2	585	-590
3	298	-308
4	51	61
5	383	370
6	430	437
7	342	340
8	219	226
9	107	96
10	11	17
	5 6 L	
1	576	523
2	672	597
3	743	764
4	469	470
5	369	361
6	72	67
7	56	-50
8	170	-175
9	169	-177
10	159	-147
	5 7 L	
0	1076	862
1	738	677
2	404	398
3	64	47
4	188	-183
5	354	-353
6	396	-393
7	329	-321
8	191	-197
9	75	-65
	5 8 L	
1	237	-210
2	384	-371
3	507	-534
4	444	-459
5	340	-349
6	118	-112
7	0	19
8	123	123
9	144	141
	5 9 L	
0	658	-552
1	535	-494
2	337	-326
3	95	-100
4	97	104
5	239	256
6	293	299
7	266	276
8	188	190
	5 10 L	
1	362	325
2	505	486
3	470	467
4	374	392
5	252	279
6	105	104
7	53	-44
8	143	-155
	5 11 L	
0	724	650
1	552	508
2	247	245
3	68	-25
4	159	-154
5	212	-228
6	237	-254
7	212	-233
	5 12 L	
1	116	-123
2	253	-254
3	366	-381
4	356	-369
5	269	-275
6	107	-102
	5 13 L	
0	402	-414
1	351	-350
2	286	-279
3	57	-44
4	127	127
5	223	236
	5 14 L	
1	177	188
2	312	314
3	347	359
	6 0 L	
0	878	-712
1	663	-614
2	650	-604
3	258	-245
4	107	105
5	391	399
6	424	459
7	352	363
8	239	238
9	126	101
10	54	20
	6 1 L	
1	599	558
2	741	684
3	664	623
4	483	438
5	364	392
6	184	186
7	0	24
8	153	-145
9	190	-173
10	185	-158
	6 2 L	
0	1506	1261
1	803	731
2	523	488
3	38	-22
4	181	-164
5	354	-344
6	455	-455
7	364	-371
8	268	-255
9	78	-59
10	34	0
	6 3 L	
1	492	-453
2	722	-705
3	857	-800
4	638	-586
5	416	-382
6	105	-93
7	62	60
8	199	185
9	207	191
10	181	161
	6 4 L	
0	931	-744
1	600	-536
2	525	-540
3	174	-159
4	112	96
5	347	337
6	424	424
7	341	344
8	242	250
9	107	99
10	11	8
	6 5 L	
1	503	466
2	664	698
3	607	620
4	458	460
5	297	284
6	135	126
7	25	-9
8	121	-126
9	169	-163
10	179	-157
	6 6 L	
0	974	789
1	691	621
2	408	406
3	91	70
4	146	-153
5	326	-322
6	360	-371
7	306	-316
8	209	-212
9	83	-77
	6 7 L	
1	181	-157
2	407	-391
3	545	-569
4	538	-556
5	351	-352
6	117	-107
7	64	50
8	140	142
9	164	159
	6 8 L	
0	842	-683
1	629	-569
2	412	-403
3	75	-48
4	205	222
5	350	347
6	294	306
7	216	215
8	157	165
	6 9 L	
1	270	240
2	410	405
3	518	529
4	434	456
5	327	329
6	79	88
7	71	-62
8	164	-155
	6 10 L	
0	669	591
1	485	440
2	262	250
3	76	36
4	41	-74
5	180	-192
6	270	-278
7	251	-265
	6 11 L	
1	255	-237
2	338	-339
3	365	-374
4	291	-301
5	253	-256
6	105	-118
7	63	-7
	6 12 L	
0	483	-487
1	441	-427
2	303	-282
3	82	-51
4	132	149
5	259	243
6	256	265
	6 13 L	
1	185	195
2	344	340
3	401	405
4	311	322
	6 14 L	
0	267	307
1	264	277
2	194	201
	7 0 L	
1	550	501
2	752	691
3	863	913
4	534	489
5	353	339
6	0	32
7	20	-28
8	135	-134
9	159	-153
10	164	-152
	7 1 L	
0	915	711
1	739	668
2	575	533
3	247	222
4	149	-124
5	411	-414
6	475	-481
7	377	-394
8	232	-220
9	93	-62
10	45	25
	7 2 L	
1	373	-346
2	593	-577
3	744	-723
4	564	-538
5	375	-354
6	105	-94
7	41	19
8	140	132
9	168	166
10	108	168
	7 3 L	
0	837	-653
1	702	-640
2	647	-627
3	153	-140
4	158	153
5	345	339
6	335	338
7	289	291
8	199	199
9	134	121
10	67	39
	7 4 L	
1	408	373
2	555	551
3	633	641
4	530	522
5	420	401
6	123	123
7	76	-63
8	194	-192
9	191	-179
	7 5 L	
0	1241	1002
1	803	724
2	346	332
3	74	-31
4	171	-172
5	317	-309
6	386	-394
7	358	-360
8	234	-221
9	60	-51
	7 6 L	
1	353	-316
2	471	-451
3	520	-532
4	414	-406
5	363	-349
6	161	-149
7	16	-13
8	137	142
9	166	176
	7 7 L	
0	910	-612
1	557	-497
2	406	-395
3	86	-61
4	160	162
5	265	277
6	267	267
7	205	212
8	103	100
9	131	114
	7 8 L	
1	191	171
2	390	378
3	565	568
4	504	511
5	318	323
6	49	66
7	78	-69
8	152	-146
	7 9 L	
0	785	648
1	597	515
2	328	318
3	48	36
4	147	-157
5	275	-285
6	297	-311
7	248	-252
8	163	-166
	7 10 L	
1	285	-265
2	416	-415
3	395	-397
4	319	-326
5	232	-225
6	110	-103
7	41	11
	7 11 L	
0	386	-377
1	362	-340
2	316	-292
3	157	-130
4	72	59
5	220	225
6	274	284
	7 12 L	
1	220	206
2	365	357
3	406	404
4	315	327
5	194	192
	7 13 L	
0	394	412
1	325	334
2	224	219
3	0	46
	7 14 L	
1	171	-199
	8 0 L	
0	1044	826
1	670	611
2	432	388
3	99	75
4	116	-100
5	297	-286
6	375	-392
7	346	-358
8	249	-235
9	88	-69
10	0	13
	8 1 L	
1	557	-464
2	771	-743
3	751	-739
4	551	-521
5	284	-276
6	95	-68
7	69	50
8	155	151
9	170	178
	8 2 L	
0	935	-670
1	617	-553
2	567	-559
3	147	-149
4	194	199
5	413	403
6	372	383
7	254	260
8	186	200
9	110	99
	8 3 L	
1	128	109
2	314	301
3	594	601
4	583	574
5	438	422
6	131	111
7	50	-38
8	141	-141
9	157	-155
	8 4 L	
0	1121	922
1	716	650
2	361	348
3	54	-41
4	190	-198
5	308	-301
6	320	-327
7	266	-267
8	199	-194
9	109	-93
	8 5 L	
1	393	-346
2	504	-493
3	534	-544
4	431	-443
5	359	-359
6	146	-131
7	64	46
8	169	178
9	175	173
	8 6 L	
0	793	-615
1	593	-533
2	352	-343
3	94	-91
4	120	120
5	277	281
6	317	329
7	288	294
8	195	192
	8 7 L	
1	308	265
2	479	453
3	541	540
4	433	433
5	287	279
6	76	83
7	40	-32
8	117	-124
	8 8 L	
0	760	565
1	590	489
2	318	296
3	69	45
4	114	-121
5	250	-252
6	275	-287
7	259	-259
8	166	-171
	8 9 L	
1	319	-269
2	408	-386
3	409	-408
4	315	-307
5	236	-244
6	124	-107
7	48	-8
	8 10 L	
0	466	-442
1	426	-388
2	315	-295
3	109	-100
4	47	80
5	229	230
6	271	296
	8 11 L	
1	239	225
2	398	390
3	474	476
4	343	350
5	176	189
	8 12 L	
0	330	351
1	314	316
2	266	253
3	109	93
4	87	-76
	8 13 L	
1	125	-146
2	227	-231
	9 0 L	
1	421	-386
2	532	-499
3	579	-554
4	440	-417
5	398	-389
6	170	-157
7	34	23
8	195	193
9	194	194
	9 1 L	
0	876	-694
1	597	-535
2	293	-267
3	82	-66
4	137	116
5	252	255
6	304	314
7	280	292
8	237	227
9	108	101
	9 2 L	
1	274	238
2	463	455
3	609	594
4	515	499
5	338	316
6	103	90
7	19	-31
8	118	-124
9	152	-151
	9 3 L	
0	1017	916
1	747	665
2	417	397
3	0	21
4	250	-243
5	378	-375
6	351	-353
7	254	-264
8	167	-169
9	38	-71
	9 4 L	
1	265	-234
2	452	-429
3	506	-512
4	493	-492
5	348	-347
6	137	-136
7	76	47
8	151	163
9	160	171
	9 5 L	
0	556	-530
1	481	-431
2	359	-339
3	109	-103
4	78	80
5	224	226
6	269	290
7	232	255
8	207	204
	9 6 L	
1	229	271
2	439	477
3	546	556
4	421	426
5	231	229
6	67	40
7	54	-41
8	98	-93
	9 7 L	
0	700	542
1	531	456
2	403	397
3	124	121
4	110	-122
5	316	-326
6	374	-381
7	266	-277
8	160	-156
	9 8 L	
1	356	-302
2	444	-420
3	406	-405
4	314	-313
5	257	-254
6	132	-122
7	52	10
	9 9 L	
0	533	-530
1	440	-379
2	233	-224
3	47	-37
4	65	62
5	146	159
6	274	235
	9 10 L	
1	225	198
2	372	354
3	423	419
4	346	346
5	201	210
6	67	59
	9 11 L	
0	389	404
1	376	369
2	277	272
3	113	71
4	111	-125
	9 12 L	
1	138	-145
2	267	-258
3	316	-321
	10 0 L	
0	932	-794
1	477	-436
2	324	-313
3	70	23
4	211	206
5	291	296
6	296	295
7	258	263
8	175	188
	10 1 L	
1	224	214
2	378	379
3	496	495
4	444	437
5	323	318
6	107	115
7	0	-16
8	98	-115
	10 2 L	
0	702	579
1	554	493
2	351	337
3	134	110
4	81	-90
5	276	-267
6	324	-338
7	299	-294
8	180	-185
	10 3 L	
1	445	-393
2	556	-525
3	538	-537
4	372	-367
5	301	-295
6	121	-102
7	44	29
8	137	156
	10 4 L	
0	814	-644
1	570	-508
2	324	-306
3	50	-40
4	122	125
5	249	245
6	279	298
7	267	275
8	200	196
	10 5 L	
1	254	229
2	420	401
3	521	533
4	389	402
5	262	259
6	31	59
7	10	-19
8	104	-100
	10 6 L	
0	498	414
1	458	413
2	391	376
3	179	157
4	112	-105
5	298	-301
6	308	-318
7	229	-243
	10 7 L	
1	285	-251
2	405	-398
3	443	-435
4	343	-342
5	231	-223
6	81	-72
7	0	21
	10 8 L	
0	571	-512
1	491	-418
2	268	-235
3	35	-44
4	101	91
5	191	207
6	254	264
	10 9 L	
1	234	199
2	370	337
3	410	401
4	373	360
5	272	258
6	121	91
	10 10 L	
0	474	461
1	410	382
2	280	244
3	26	28
4	128	-130
5	212	-211
	10 11 L	
1	132	-121
2	233	-226
3	328	-304
	10 12 L	
0	391	-414
1	304	-325
	11 0 L	
1	155	145
2	343	329
3	502	505
4	467	458
5	304	299
6	87	79
7	65	-35
8	106	-114
	11 1 L	
0	704	577
1	516	467
2	412	395
3	121	98
4	150	-153
5	322	-323
6	330	-337
7	219	-238
8	161	-152
	11 2 L	
1	388	-346
2	531	-518
3	515	-518
4	387	-387
5	247	-242
6	89	-66
7	48	50
8	91	124
	11 3 L	
0	528	-494
1	431	-385
2	298	-273
3	121	-109
4	40	26
5	182	183
6	291	307
7	285	300
8	196	196
	11 4 L	
1	307	268
2	431	413
3	414	408
4	319	333
5	234	239
6	120	123
7	27	9
	11 5 L	
0	707	589
1	569	503
2	343	324
3	43	40
4	175	-195
5	295	-302
6	276	-293
7	215	-223
	11 6 L	
1	235	-201
2	379	-364
3	449	-457
4	389	-392
5	260	-252
6	78	-68
7	43	46
	11 7 L	
0	488	-440
1	394	-356
2	266	-235
3	76	-63
4	0	62
5	170	171
6	217	231
	11 8 L	
1	215	192
2	319	304
3	373	371
4	296	310
5	229	235
	11 9 L	
0	488	487
1	431	417
2	279	259
3	66	22
4	164	-156
	11 10 L	
1	119	-111
2	240	-232
3	277	-349
	11 11 L	
0	342	-361
1	294	-304
	12 0 L	
0	495	433
1	437	410
2	310	309
3	115	101
4	106	-114
5	244	-244
6	240	-249
7	204	-211
	12 1 L	
1	247	-218
2	409	-402
3	493	-507
4	406	-419
5	245	-245
6	72	-42
7	78	62
	12 2 L	
0	595	-498
1	483	-431
2	319	-304
3	125	-103
4	84	95
5	244	260
6	300	314
7	258	265
	12 3 L	
1	275	261
2	417	392
3	411	416
4	314	316
5	226	226
6	99	92
7	0	-7
	12 4 L	
0	598	498
1	462	417
2	306	294
3	0	51
4	125	-124
5	242	-246
6	240	-265
	12 5 L	
1	161	-151
2	293	-285
3	407	-403
4	379	-373
5	283	-280
6	84	-89
	12 6 L	
0	597	-537
1	448	-405
2	229	-214
3	62	14
4	105	111
5	164	184
6	212	222
	12 7 L	
1	257	227
2	375	348
3	343	362
4	309	306
5	213	225
	12 8 L	
0	441	433
1	395	368
2	272	243
3	65	46
4	73	-111
	12 9 L	
1	106	-115
2	267	-245
3	343	-329
	12 10 L	
0	310	-328
1	277	-289
	13 0 L	
1	245	-232
2	375	-376
3	402	-428
4	335	-348
5	223	-236
6	65	-75
	13 1 L	
0	592	-506
1	424	-396
2	242	-245
3	69	-32
4	99	102
5	183	190
6	208	239
	13 2 L	
1	204	186
2	286	297
3	352	352
4	281	307
5	239	243
6	106	104
	13 3 L	
0	547	482
1	448	417
2	292	283
3	71	51
4	121	-143
5	236	-257
6	216	-254
	13 4 L	
1	184	-166
2	313	-329
3	438	-444
4	374	-392
5	226	-230
	13 5 L	
0	439	-410
1	387	-359
2	235	-229
3	107	-56
4	60	95
5	178	197
	13 6 L	
1	197	167
2	272	259
3	303	304
4	282	282
	13 7 L	
0	458	461
1	395	376
2	230	206
3	0	24
	13 8 L	
1	210	-203
2	335	-330
	14 0 L	
0	568	-498
1	423	-406
2	253	-247
3	0	-34
4	113	128
5	219	241
	14 1 L	
1	189	171
2	295	273
3	290	310
4	299	309
5	243	261
	14 2 L	
0	556	484
1	408	378
2	207	191
3	19	-14
4	85	-101
5	129	-156
	14 3 L	
1	198	-173
2	323	-319
3	374	-383
4	313	-323
	14 4 L	
0	396	-367
1	355	-324
2	268	-262
3	105	-84
4	87	94
	14 5 L	
1	196	178
2	312	292
3	337	338
	14 6 L	
0	410	416
1	344	335
2	238	210
	14 7 L	
1	166	-167
	15 0 L	
1	151	145
2	237	245
3	293	309
	15 1 L	
0	481	447
1	378	359
2	195	193
3	47	14
	15 2 L	
1	201	-185
2	291	-305
3	346	-365
	15 3 L	
0	340	-345
1	313	-300
2	227	-216
	15 4 L	
1	184	178

[a] The F_c values for unobserved reflections are zero.

form a square 2.73 (1) Å on edge on the other side of Er which is rotated 45° with respect to the large square. The $H_2O(1)$ molecule caps the large square. A stereoscopic drawing of the environment around Er is shown in Figure 1. The cation and $H_2O(1)$ lie on the fourfold axis and one oxygen atom from each COO group of each molecule is bonded to erbium. The bond lengths between erbium and oxygen atoms (Table III) are nearly equal to the sum of the ionic radii. The "statistical oxalate ion" is planar within experimental error and has mmm symmetry similar to the configuration of oxalate in weddellite, $CaC_2O_4 \cdot (2 + x)H_2O$.[15] The dimensions and angles determined for the anion in this investigation agree with those found in weddellite. Figure 2 illustrates the hydrogen bonding between the water molecules and the oxygen atoms of the statistical oxalate molecule. The water molecule, $H_2O(2)$, is in

---

(15) C. Sterling, *Acta Crystallogr.*, **18**, 917 (1965).

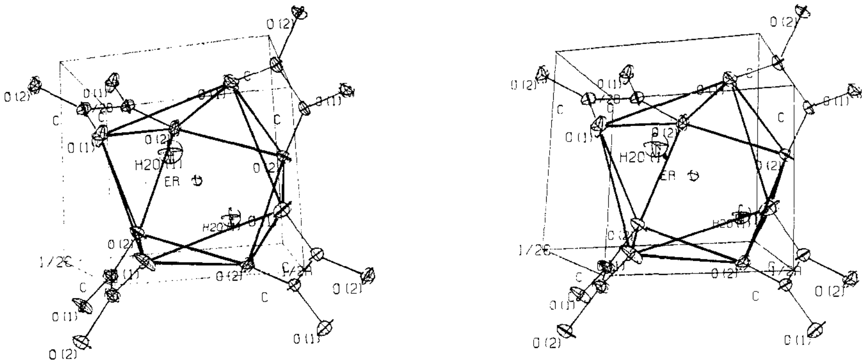

Figure 1.—The structure of $Er(C_2O_4)(HC_2O_4)\cdot 3H_2O$ showing the environment about Er. The antiprism and one-fourth unit cell are outlined.

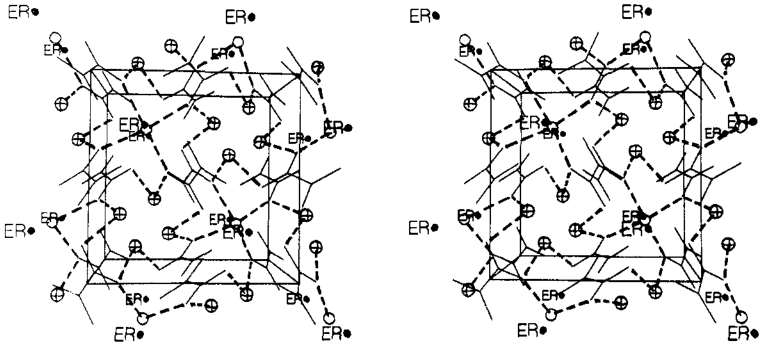

Figure 2.—The unit cell content for $Er(C_2O_4)(HC_2O_4)\cdot 3H_2O$. The origin is in the lower right-hand corner, the vertical axis is *a*, the horizontal axis is *b*, and the *c* axis points to the observer. The oxalate ion is shown by the solid lines, $H_2O(1)$ by open circles, and $H_2O(2)$ by circles with crosses. Hydrogen bonding is indicated by the dashed lines.

TABLE III

BOND DISTANCES AND ANGLES IN $Er(C_2O_4)(HC_2O_4)\cdot 3H_2O$[a]

Atoms	Distance, Å	Atoms	Distance, Å
Er–O(1)	2.362 (5)[b]	O(2)–$H_2O(2)$	2.656 (15)
Er–O(2)	2.418 (5)	O(2)–$H_2O(1)$	3.180 (9)
Er–$H_2O(1)$	2.441 (9)	C–C	1.529 (11)
O(1)–C	1.265 (7)	$H_2O(2)$–$H_2O(2)$	1.867 (25)
O(1)–$H_2O(2)$	2.656 (14)	$H_2O(2)$–$H_2O(2)$	2.425 (37)
O(1)–$H_2O(1)$	2.726 (7)	O(1)–O(1)[d]	3.121 (7)
O(2)–C	1.254 (7)	O(2)–O(2)[d]	2.731 (7)

Atoms	Angle, deg
O(1)–C–O(2)	125.9 (5)
O(1)–C–C	116.8 (7)
O(2)–C–C	117.3 (6)

[a] Numbers in parentheses are standard deviations. [b] Calculated by the ORFFE[c] program using the variance–covariance matrix from ORFLS.[11] [c] W. R. Busing, K. O. Martin, and H. A. Levy, USAEC Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964. [d] Edge of square around Er.

general position 8(g) and half of a molecule occupies this site. A hydrogen bond exists between two equivalent molecules at 2.43 (3) Å which is not indicated in Figure 2; the very short distance of 1.87 (3) Å is between a molecule and its "ghost" due to the disordered arrangement. It is difficult to assess the physical significance of the anomalously short 2.43-Å hydrogen bond because of the half-occupancy of this site by $H_2O(2)$. Each $H_2O(2)$ molecule has two additional hydrogen bonds 2.66 (2) Å long which go to the double- and single-bonded oxygen atoms. The equivalence of these lengths is most likely due to the disordered arrangement of the oxalate molecule.

The water molecule $H_2O(1)$, at the center of a distorted square antiprism formed by oxygen atoms of the oxalate molecules, is hydrogen bonded to four O(1) atoms at 2.73 (1) Å, but makes only van der Waals contact with the other four O(2) atoms.

The space group as determined from room-temperature X-ray diffraction spectra forces a solution of this structure in which the oxalate and bioxalate ions must be disordered. This disorder cannot be due only to the inability of the X-ray technique to detect the hydrogen atoms in this structure since in an ordered structure the difference in bond distances within the bioxalate between the COO group and COOH would have been observed. The space group would also have been of lower symmetry in such an ordered structure and there would be no need for the statistical distribution of $H_2O(2)$. It is possible that at a low temperature ordering takes place but this possibility was not investigated.