Structural Studies on the Rare Earth Carboxylates

18. The Crystal and Molecular Structure of Hexa-aquo Tris-malonato Di-neodymium(III)

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The crystal and molecular structure of $Nd_2(C_3H_2O_4)_3.6H_2O$ has been determined from three-dimensional, photographic, X-ray intensity data. Four formula units crystallize in a monoclinic unit cell with the dimensions $a = 11.210(2)$ Å, $b = 12.383(2)$ Å, $c = 13.696(3)$ Å, and $\beta = 93.01(2)°$. The space group is $I2/a$. The neodymium malonate hexahydrate is metastable and passes into the corresponding octahydrate when stored in the mother liquor. The structure is a three-dimensional neodymium-malonate network and is closely related to that of the octahydrate. The neodymium ion is coordinated by six carboxylate and three water oxygens forming a distorted monocapped square antiprism. The $Nd-O$ bond distances are in the range $2.35-2.61$ Å. One of the two independent malonate ions has strict twofold symmetry. The two oxygens of its carboxylate group are bonded to the same neodymium ion and one of them is also bonded to an adjacent neodymium ion. The other malonate ion forms a six-membered chelate ring with neodymium and also connects the neodymium ion with an adjacent one by a bridge of the type $Nd-OCO-Nd$. The chelate ring has a boat conformation and both malonate ions are nonplanar. The water molecules form hydrogen bonds with $O-O$ distances in the range $2.74-2.85$ Å.

This work is part of a systematic study of the structures of the lanthanoid malonate compounds $M_2mal_3 . nH_2O$ (M = lanthanoid, mal = $OOCCH_2COO^{2-}$, and $n = 6$ or 8) undertaken to get some information of the conformation of the malonate ions and the arrangement of the ligand atoms around the central ion in lanthanoid malonate complexes.

The structure of the compound $Nd_2mal_3.8H_2O$ (NDO) has been reported previously.[1] This paper deals with the structure of the compound $Nd_2mal_3.6H_2O$ (NDH) which is metastable relative to NDO at room temperature. The unit cell dimensions of NDH and NDO are closely related (see below) indicating that the two structures may be similar. With different numbers

9

of crystal water the hydrogen bond systems must, however, be different in the two compounds.

In NDO, one malonate ion forms a six-membered chelate ring with neodymium. Since very little is known about the preferred conformation of chelated malonate rings,[2] it was regarded with special interest. One of its non-chelating oxygens is bonded to an adjacent neodymium and the other oxygens are hydrogen bonded to water molecules. It must be assumed that this bonding plays an important part in determining the precise conformation of the ring, and it is then of interest to study the neodymium malonate chelate ring in a different hydrogen bond situation.

EXPERIMENTAL

The method of preparation and the habit of the crystals of NDH have been described in Ref. 1.

A crystal of the dimensions $0.10 \times 0.09 \times 0.20$ mm^3 mounted along the 0.20 mm edge was used in recording the layers $hk0-hk15$. 1869 measurable reflexions were recorded with the integrated multiple-film Weissenberg technique using Zr-filtered Mo$K\alpha$-radiation. 1520 of these reflexions were within the Cu-sphere representing 60 % of the possible number. The intensities were measured visually by comparison with a calibrated scale. The data were corrected for Lorentz, polarisation, and absorption effects. The linear absorption coefficient is 55 cm^{-1} and the transmission factors evaluated by numerical integration were in the range $0.58-0.62$.

UNIT CELL AND SPACE GROUP

The crystals of NDH are monoclinic. The unit cell is C-centered with $a = 18.15$ Å, $b = 12.38$ Å, $c = 11.21$ Å, and $\beta = 131.1°$. $Z = 4$. The alternative choice of axis along [001], [010], and [$\bar{1}0\bar{1}$] results in a bodycentered cell with $a = 11.210(2)$ Å, $b = 12.383(2)$ Å, $c = 13.696(3)$ Å, and $\beta = 93.01(2)°$. This cell is similar to that of NDO which is orthorhombic with $a = 11.26$ Å, $b = 12.60$ Å, and $c = 14.69$ Å, and was chosen for the description in order to facilitate the comparison between the two structures. The accurate values of the cell parameters were determined from powder data by least squares refinement as described before.[3] Table 1 gives the experimental values of $\sin^2 \theta$ together with those calculated in the last cycle of refinement.

The systematically absent reflexions are hkl: $h+k+l \neq 2n$ and $h0l$: $h \neq 2n$. The possible space groups are then Ia and $I2/a$. The concentration of peaks in the Patterson section $P(x0z)$ indicated the space group $I2/a$. The structure was accordingly assumed to be centrosymmetric and the subsequent refinements gave no reason for changing this assumption. The general position of the space group $I2/a$ is eightfold: $(0,0,0;1/2,1/2,1/2) \pm (x,y,z; \bar{x},y,1/2-z)$. The conventional space group corresponding to $I2/a$ is $C2/c$. The transformation of indices from the bodycentered to the C-centered cell is given by $(h,k,l) = (-1,0,-1/0,1,0/1,0,0)(h',k',l')$ where h',k',l' refer to the body centered cell.

Table 1. Powder data for $Nd_2(C_3H_2O_4)_3.6H_2O$. 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}
0 1 1	704	705	vvw	2 2 4	8869	8856	vw
1 1 0	860	862	s	−1 3 4		8882	
0 0 2	1267	1271	vs	−3 1 4	9250	9250	w
0 2 0	1547	1550	s	−1 4 3	9421	9412	vw
−1 1 2	2050	2051	s	2 4 2	9529	9531	vvw
−1 2 1	2380	2383	s	1 2 5	10166	10170	w
−2 1 1	2516	2521	s	3 1 4	10242	10227	vvw
2 1 1	2683	2684	s	−3 4 1	10675	10665	w
0 1 3	3242	3247	vvw	4 1 3	11338	11323	w
2 0 2	3331	3331	w	−1 5 2		11352	
3 1 0	4648	4656	m	0 3 5	11426	11430	vw
2 2 2	4886	4881	vw	−4 0 4	12011	12020	w
1 2 3	5003	5006	m	−1 1 6	12069	12054	w
−1 3 2	5152	5152	vw	1 1 6	12545	12542	w
2 1 3	5379	5388	m	−2 0 6	12861	12845	w
−2 3 1	5618	5621	m	−3 2 5	13163	13150	w
−3 2 1	6006	6014	w	2 4 4	13495	13506	m
3 1 2	6168	6171	m	−5 2 1		13521	
0 3 3	6340	6347	w	5 1 2		13922	
−1 4 1	6954	6952	w	5 2 1	13935	13928	s
2 0 4	7293	7305	vw	0 6 0		13952	
0 4 2	7483	7472	m	3 5 0		13957	
3 3 0	7767	7756	vvw	4 3 3	14429	14423	w
−2 3 3	7998	8000	w	−3 5 2	14974	14984	w
−3 2 3	8309	8311	m	−1 5 4	15074	15083	m
4 1 1	8464	8456	m	0 6 2	15224	15223	vw
−4 0 2	8528	8533	vvw	3 5 2	15476	15472	w
−3 3 2	8764	8783	vvw	−5 2 3	15668	15655	vw

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The structure of NDH was determined by the heavy atom method. A three-dimensional Patterson synthesis revealed the position of neodymium and the positions of the remaining 14 non-hydrogen atoms were obtained from the subsequent difference electron density calculation.

The preliminary atomic coordinates, isotropic temperature factors, and inter layer scale factors were improved by least squares refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights, w, were chosen according to Cruickshank [4] and only the reflexions with $0.80 \leq |F_o|/|F_c| \leq 1.25$ were included in the refinement. The atomic scattering factors for the neutral atoms were for carbon and oxygen taken from International Tables [5] and for neodymium from Cromer *et al.*[6]

The discrepancy indexes $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{\frac{1}{2}}$ converged to 0.094 and 0.098, respectively. All the observed reflexions were included in the calculation of R. Further refinement, now with anisotropic thermal parameters for neodymium and an over all scale-

factor, resulted in $R = 0.084$ and $wR = 0.088$. In the last cycle of refinement the shifts of all parameters were less than 1 % of their estimated standard deviations.

The approximate constancy of the averages of $w(|F_o| - |F_c|)^2$ between different $|F_o|$ and $\sin \theta$ intervals indicated that the weighting scheme used was reasonable. (Table 2).

Table 2. Analysis of the weighting scheme $w = 1/(10 + |F_o| + 0.01|F_o|^2)$. The averages $\overline{w\varDelta^2}$, where $\varDelta = |F_o| - |F_c|$, are normalized.

Interval F_o	Number of reflexions	$\overline{w\varDelta^2}$	Interval $\sin \theta$	Number of reflexions	$\overline{w\varDelta^2}$
0 − 62	155	1.00	0.00 − 0.28	328	1.10
62 − 71	172	0.91	0.28 − 0.35	303	0.98
71 − 78	166	1.11	0.35 − 0.40	269	0.99
78 − 85	168	0.99	0.40 − 0.44	209	0.98
85 − 94	170	1.05	0.44 − 0.48	191	0.93
94 − 106	175	1.05	0.48 − 0.51	166	0.83
106 − 121	179	1.12	0.51 − 0.53	105	1.02
121 − 142	179	1.03	0.53 − 0.56	80	1.25
142 − 177	182	0.74	0.56 − 0.58	37	1.11
177 − 446	184	1.00	0.58 − 0.60	24	0.81

Table 3. Atomic parameters with estimated standard deviations for the compound $Nd_2(H_2C_3O_4)_3 \cdot 6H_2O$.

Atom	Group	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$B/Å^2$
Nd		1537.1(5)	1020.4(5)	335.1(5)	$(1.14)^a$
O(1)	COO⁻	1404(10)	78(10)	1990(9)	2.5(2)
O(2)	COO⁻	− 3(7)	− 405(8)	898(7)	1.3(1)
O(3)	COO⁻	2354(9)	− 812(8)	254(8)	1.8(1)
O(4)	COO⁻	3384(11)	− 2322(11)	499(10)	2.8(2)
O(5)	COO⁻	3610(10)	1033(10)	891(8)	2.3(2)
O(6)	COO⁻	5502(13)	656(13)	1215(11)	3.5(2)
O(7)	H_2O	− 460(11)	1854(11)	674(9)	3.0(2)
O(8)	H_2O	1724(15)	2473(12)	1653(12)	4.2(3)
O(9)	H_2O	2574(10)	687(10)	− 1249(9)	2.5(2)
C(1)		0	− 1238(21)	1/4	2.9(4)
C(2)		494(11)	− 484(12)	1743(10)	1.6(2)
C(3)		3180(12)	− 1335(12)	625(11)	1.9(2)
C(4)		4134(13)	− 792(13)	1302(12)	2.1(2)
C(5)		4458(10)	383(11)	1086(9)	1.4(2)

^{a} The anisotropic thermal parameters for neodymium, calculated from the expression: $\exp\,[-(h^2\beta_{11} + 2hk\beta_{12} + ...)]$ are $\beta_{11} = 0.00234(4)$, $\beta_{22} = 0.00148(3)$, $\beta_{33} = 0.00190(3)$, $\beta_{12} = -0.00004(4)$, $\beta_{13} = -0.00023(2)$, and $\beta_{23} = 0.00009(4)$, resulting in root mean square displacements along the principal axis of the thermal ellipsoid $R_1 = 0.141$ (Å), $R_2 = 0.107$ (Å), and $R_3 = 0.116$ (Å).

Table 4. Observed and calculated structure factors in $Nd_2(C_2H_2O_4)_3.6H_2O$. The 139 reflexions not obeying the condition $0.80 \leq |F_o|/|F_c| \leq 1.25$ are denoted by asterisks. In each group the running index l, $|F_o|$, and $|F_c|$ are given.

H= 0 K=-17		
-11	79	76
-9	90	111
-7	105	105
-5	112	111
H= 0 K=-14		
-16	87	84
-14	99	93
-12	95	61*
-4	89	89
-2	156	147
H= 0 K=-13		
-11	75	74
-9	93	108
-7	153	149
-5	130	139
-3	100	109
H= 0 K=-11		
-11	99	92
-9	123	115
-7	124	133
-5	134	131
-3	114	113
H= 0 K=-10		
-18	100	82
-16	112	104
-14	96	110
-12	117	127
-10	92	80
-6	69	59
-4	186	186
-2	252	222
0	231	220
H= 0 K= -9		
-9	61	55
-7	96	98
-5	143	150
-3	116	101
H= 0 K= -8		
-12	60	46*
-10	60	51
-4	126	124
-2	90	71*
0	92	85
H= 0 K= -7		
-19	82	75
-13	79	93
-11	102	121
-9	180	171
-7	222	233
-5	173	186
-3	150	167
-1	68	75
H= 0 K= 6		
-18	78	67
-16	95	99
-14	132	131
-12	116	125
-10	95	100
-6	92	93
-4	93	98
-2	248	280
0	351	389
H= 0 K= -5		
-5	66	58
-3	94	80
H= 0 K= -4		
-18	91	80
-16	109	104
-14	121	124
-12	116	129
-10	119	113
-4	217	210
-2	351	351
0	285	277
H= 0 K= -3		
-19	85	79
-13	73	56*
-11	160	165
-9	230	198
-7	241	240
-5	330	327
-3	232	217
H= 0 K= -2		
-14	75	65
-12	74	63
-10	47	44
-8	54	56
H= 0 K= -1		
-13	71	57
-11	91	85
-9	133	109
-7	171	167
-5	121	126
H= 0 K= 0		
-18	89	95
-16	160	127
-14	173	186
-12	163	179
-10	113	115
-8	58	60
-6	59	38*
-4	82	85
H= 1 K=-18		
-11	87	71
-9	92	78
H= 1 K=-16		
-9	80	76
-3	74	52*
H= 1 K=-15		
-8	98	96
-6	123	124
-4	120	148
0	117	89*
10	121	122
12	89	97
H= 1 K=-13		
-4	77	71
-2	82	82
8	64	56
10	94	69*
H= 1 K=-12		
-15	80	80
-13	107	115
-11	170	131
-9	127	131
-7	110	106
-3	86	78
-1	165	152
5	160	165
7	92	103
13	76	67
15	80	88
17	85	82
19	89	62*
H= 1 K=-11		
-10	67	59
-8	82	89
-6	119	131
-4	149	151
-2	145	146
0	87	93
6	94	88
8	119	118
10	137	134
12	120	128
14	76	67
H= 1 K=-10		
7	65	45*
H= 1 K= -9		
-18	82	75
-14	78	59*
-10	68	68
-8	141	155
-6	203	212
-4	218	233
-2	211	210
0	107	116
4	81	64*
6	133	116
8	129	120
10	172	156
12	146	148
14	72	74
H= 1 K= -8		
-15	94	88
-13	137	133
-11	142	151
-9	152	151
-7	109	101
-1	130	140
3	254	261
5	172	179
7	123	121
9	58	51
13	67	52*
15	94	101
17	93	99
19	90	76
H= 1 K= -7		
-6	76	80
-4	112	108
-2	53	51
2	44	54
6	64	56
8	109	99
H= 1 K= -6		
-15	76	78
-13	120	121
-11	130	134
-9	122	115
-7	63	71
-3	42	46
-1	167	131*
1	241	237
3	285	262
5	114	134
7	96	82
15	83	88
17	89	88
H= 1 K= -5		
-20	82	83
-18	83	90
-16	84	93
-14	60	56
-10	70	71
-8	226	221
-6	288	317
-4	410	442
-2	320	290
0	88	100
2	41	47
4	98	89
6	159	161
8	217	214
10	274	234
12	173	181
14	153	149
16	71	59
H= 1 K= -4		
-15	87	59*
-13	80	75
-11	135	122
-9	156	143
-7	118	129
-5	47	43
-3	169	165
-1	257	266
1	128	121
3	35	42
5	67	80
7	109	96
9	71	78
13	73	71
15	67	54
H= 1 K= -3		
-8	127	115
-6	75	68
-4	216	179
-2	163	153
2	39	37
4	88	97
6	68	69
8	55	61
10	116	104
12	58	60
H= 1 K= -2		
-17	78	72
-15	122	122
-13	151	137
-11	188	176
-9	204	183
-7	200	193
-5	114	104
-3	59	66
1	154	270*
3	276	304
5	284	281
7	253	241
9	123	112
13	133	130
15	123	128
17	120	115
19	92	85
H= 1 K= -1		
-20	87	71
-18	96	100
-16	81	84
-14	62	44*
-12	56	56
-10	94	77
-8	128	105
-6	358	363
-4	446	425
6	251	241
8	292	277
10	162	180
12	143	142
14	127	110
16	74	58*
H= 2 K=-17		
-5	83	103
H= 2 K=-16		
-10	86	75
-8	90	83
-6	81	68
H= 2 K=-14		
-12	99	75*
-10	123	117
-8	144	135
-6	125	98*
8	151	130
10	104	62*
H= 2 K=-13		
-15	87	82
-13	90	84
-7	72	66
-5	138	130
-3	132	152
-1	162	160
9	98	85
11	102	104
13	108	94
15	87	79
H= 2 K=-11		
-5	135	134
-3	162	168
-1	152	145
9	90	89
11	95	104
11	113	104
H= 2 K=-10		
-14	85	65*
-12	103	112
-10	158	155
-8	163	177
-6	176	186
-4	120	112
0	106	106
4	217	200
6	213	224
8	157	171
10	134	138
H= 2 K= -9		
-13	87	72
-7	71	70
-5	80	74
-3	77	87
-1	69	70
3	65	78
11	81	73
H= 2 K= -8		
-10	82	74
-8	130	119
-6	107	97
0	105	92
2	95	91
6	108	86*
8	59	40*
10	69	49*
H= 2 K= -7		
-19	86	64*
-17	96	88
-15	124	131
-13	116	127
-11	82	83
-7	101	93
-5	174	195
-3	270	262
-1	312	332
3	157	150
5	66	62
9	173	170
11	177	174
13	148	148
15	117	112
17	81	61*
H= 2 K= -6		
-14	71	76
-12	109	110
-10	156	161
-8	177	206
-6	125	140
-4	85	88
-2	56	49
0	160	159
2	189	210
4	219	220
6	188	195
8	173	183
10	111	88*
16	86	66*
18	82	63*
20	88	59*
H= 2 K= -5		
-9	55	63
-3	48	49
3	38	28*
9	55	55
H= 2 K= -4		
-14	74	68
-12	117	124
-10	211	193
-8	267	236
-6	211	217
-4	187	205
-2	130	117
0	119	136
2	231	194
4	309	296
6	234	224
8	209	218
10	163	166
16	81	81
18	80	80
20	86	74
H= 2 K= -3		
-19	97	97
-17	107	113
-15	99	101
-13	100	119
-11	129	140
-7	144	141
-5	305	281
-3	285	299
1	303	277
3	244	228
7	60	51
9	81	75
11	162	165
13	170	180
15	109	112
17	83	74
H= 2 K= -2		
-12	78	64
-10	70	77
-8	67	69
-6	146	143
2	122	127
4	207	188
6	199	181
8	81	77
H= 2 K= -1		
-19	81	55*
-17	81	70
-15	81	75
-13	74	67
-11	87	88
-9	50	38*
-7	97	91
-5	146	131
3	206	206
5	141	122
9	123	117
11	116	136
13	123	141
15	90	87
H= 2 K= 0		
-20	77	54*
-14	78	88
-12	217	227
-10	287	276
-8	300	313
-6	206	182
-4	111	116
4	233	232
6	408	420
8	257	283
10	119	134
16	72	77
18	102	99
20	101	96
H= 3 K=-19		
-2	81	75
0	88	97
4	98	84
H= 3 K=-18		
-7	81	84
-5	87	73
-3	79	75
5	80	77
7	82	76
9	84	69
11	86	68*
H= 3 K=-16		
-9	78	80
-7	83	94
-5	74	76
5	96	88
7	76	84
9	79	74
11	82	69
H= 3 K=-15		
-14	99	88
-12	95	98
-10	92	83
-2	116	110
0	128	136
2	147	150
4	131	133
6	72	77
H= 3 K=-14		
-5	68	74
7	71	67
H= 3 K=-13		
-12	89	80
-10	78	57*
-2	74	70
2	81	87
4	83	76
6	67	51*
H= 3 K=-12		
-11	77	83
-9	136	141
-7	170	174
-5	157	153
-3	78	97
-1	84	87
3	66	66
5	122	130
7	138	148
9	144	143
11	132	128
13	75	81
H= 3 K=-11		
-14	81	76
-12	70	77
-10	93	81
-4	82	90
-2	125	132
0	189	185
4	114	124
6	66	63
12	77	71
14	82	84
H= 3 K=-10		
-1	53	61
3	77	68
5	96	88
H= 3 K= -9		
-16	98	93
-14	99	110
-12	110	114
-10	86	91
-8	62	66
-6	80	83
-2	132	150
0	200	212
2	181	190
4	216	185
6	144	133
12	86	85
14	100	99
16	76	89
H= 3 K= -8		
-11	79	96
-9	149	167
-7	219	217
-5	219	239
-3	132	182*
-1	95	84
5	133	138
7	208	220
9	238	226
11	132	125
H= 3 K= -7		
0	43	45
2	89	89
H= 3 K= -6		
-9	145	128
-7	167	176
-5	163	177
-3	91	79
-1	101	85
1	97	91
3	42	43
5	147	164
7	155	171
9	202	180
11	109	93
H= 3 K= -5		
-18	75	64
-16	107	115
-14	131	146
-12	149	153
-10	153	157
-8	62	66
-6	56	58
-4	141	129
-2	265	282
0	308	306
2	346	398
4	284	279
6	122	117
10	91	95
12	145	144
14	133	146
16	132	127
H= 3 K= -4		
-11	84	83
-9	100	75*
-7	82	67
-5	170	167
-3	323	281
-1	154	152
1	42	36
5	61	73
7	156	162
9	127	125
11	94	85
H= 3 K= -3		
-14	62	71
-10	60	60
-6	56	46
-2	174	155
2	76	59*
4	92	79
6	68	41
8	46	44
H= 3 K= -2		
-21	81	68
-19	82	74
-17	83	88
-15	64	72
-11	117	129
-9	227	211
-7	234	244
-5	325	345
3	45	49
5	197	185
7	252	284
9	212	254
11	148	158
13	92	95
H= 3 K= -1		
-18	72	53*
-16	94	81
-14	124	121
-12	209	199
-10	130	117
-6	164	144
-4	257	226
4	223	211
6	177	153
10	50	49
12	155	139
14	131	138
H= 4 K=-17		
1	110	104
3	101	122
5	113	115
7	106	92
H= 4 K=-16		
-4	90	87
-2	89	90
H= 4 K=-14		
-6	120	115
-4	152	150
-2	157	154
0	96	110
8	89	78
10	109	108
12	96	98
H= 4 K=-13		
-13	94	89
-11	106	113
-9	93	99
-7	98	90
-1	83	73
1	142	126
3	151	148
5	135	147
7	118	121
9	87	64*
H= 4 K=-11		
-13	88	84
-11	99	99
-9	94	72*
-7	69	71
-1	82	76
1	139	136
3	131	136
5	123	127
7	90	96
9	80	54*
H= 4 K=-10		
-16	94	88
-14	88	79
-8	113	108
-6	176	169
-4	185	188
-2	195	214
0	185	204
2	78	76
6	109	115
8	115	144*
10	102	124
12	141	127
14	90	97
H= 4 K= -9		
-11	77	86
-9	102	102
-7	96	89
3	145	147
5	127	126
7	82	82
9	67	64
H= 4 K= -8		
-6	63	59
-2	118	114
0	162	163
2	69	67
8	88	83
12	79	83
H= 4 K= -7		
-13	111	132
-11	174	182
-9	215	205
-7	130	140
-5	58	69
-1	117	116
1	229	201
3	269	264
5	262	265
7	197	189
9	96	96
17	93	96
H= 4 K= -6		
-16	87	76
-14	74	51*
-8	114	106
-6	119	120
-4	163	161
-2	222	213
0	153	150
2	131	129
6	106	93
8	179	165
10	139	166
12	116	112
14	98	97
H= 4 K= -5		
-5	51	51
-3	46	63*
-1	41	48
H= 4 K= -4		
-16	100	102
-14	77	76
-8	149	165
-6	159	166
-4	215	222
-2	192	257*
0	186	180
2	202	183
4	78	66
6	131	143
8	147	163
10	164	171
12	112	131
14	79	105*
16	86	71
H= 4 K= -3		
-15	79	100*
-13	147	160
-11	139	177*
-9	196	198
-7	190	191
-5	161	132
-3	50	37*
3	278	406*
5	386	359
7	160	183
9	117	108
17	88	94
H= 4 K= -2		
-6	94	98
-4	177	172
10	89	82
12	76	67
H= 4 K= -1		
-13	92	109
-11	118	134
-9	179	193
-7	152	140
5	177	182
7	95	84
H= 4 K= 0		
-20	96	66*
-18	115	103
-16	97	101
-14	88	77
-10	85	56*
-8	98	96
-6	240	262
-4	327	321
4	55	50
6	95	92
8	223	247
10	207	230
12	217	219
H= 5 K=-18		
-3	86	73
-1	84	92
1	84	91
3	85	76
H= 5 K=-16		
-3	92	72*
-1	100	94
1	92	88
3	72	66
H= 5 K=-15		
-8	112	127
-6	119	133
-4	116	102
2	74	67
4	107	110

EVA HANSSON

Table 4. Continued.

```
  6  120  126      -5  129  113      -7   75   67     H=   6 K=  0      1  113  111      9   76   45     H=   9 K=-11     H= 19 K=-16
  8   80 115*      -3  11R  109      -5  12R  124     -16   97  103      3  155  153     11   90   82    -12   73   75     -4   73   57*
 1L   99   86      -1  174  170      -3  171  157     -14  119  115      5  146  134     13   98  108    -10   70   72
                    1  218  212      -1  110   94     -12  127  121      7  110  115     15  105  104     -8   66   64     H= 10 K=-14
 H=   5 K=-14       3  176  15R       5   72   67     -10  163  162      9   83   77                     -6   83   78     -4   88   81
  1   70.  67       5  109  109       7   59   66      -8  173  182                     H=   8 K=  0      0  118  105      0   71   60
                    9   65   60       9  122  104      -6  145  129     H=   7 K= -3    -10   88   88      2  131  122     12   72   67
 H=   5 K=-13      11   72   72      11  103   88      -4  104   84      -6   99   91     -8  121  139      4  106  100     14   68   66
 -8   73   75      13   86   86                       -2  123  213*     -4  120  104     -6  116  104      6   65   72
 -6   77   89      15   72   78      H=   6 K= -8       2  156  279*     -2   76   69     -4  127  125                     H= 10 K=-13
 -4   65   69                       -12   78   78      4  291  300       2   64   62     -2  139  122     H=   9 K= -8    -11   73   66
  4   69   72      H=   5 K= -3     -10   72   81      6  182  180       4   58   45*     4  102   93    -12   89   98     -9   84   79
                   -8   81   74      -8   57   51                       10   86   84      6  131  130    -10   91   93     -7   81   88
 H=   5 K=-12      -6   71   75      -2   69   47     H=   7 K=-1R                        8  132  154     -8   79   71     -5   66   68
-17   96   73*     -4  124  118      0  156  15R       3   90   75     H=   7 K= -2     10  109  111     -6   63   63      7   82 104*
-15   91   80      -2  111  102      2  121  110                      -13  102  113                      0  114  112      9   72   75
-13   94   86       2   72   57*     4   51   48     H=   7 K=-15     -11  164  173     H=   8 K= -5      2  166  167     11   63   69*
-11   82   73       4  190  167      6   59   68     -16  106   78*    -9  189  192     -3   56   51      4  137  139
 -5   72   86       6  126  118                      -14  123  111     -7  185  197      3   53   54      6  112  110     H= 10 K=-11
 -3  170  160       8   84   92     H=   6 K= -7      -2  111  132     -5   98   92                       8   74   76    -11   57   54
 -1  175  199                      -19   82   79       0  101  109      1  125  120     H=   8 K= -4                     -9   92   73*
  1  176  196      H=   5 K=-11     -17   84   81      2   86   81      3  223  227    -10   99  116     H=   9 K= -6    -7   98   80
  3  144  139     -12   97   82      -9  120  114                       5  227  261     -8  183  176     -9   78   80    -5  108  79*
  9   73   67     -10  100   93      -7  184  188     H=   7 K=-14      7  235  256     -6  177  174     -7  120  134      5   96   96
 11   99  101      -8   95   97      -5  236  224      1   82   53*     9  168  168     -4  177  173     -5  135  137      7   74   79
 13   96  107      -6   91  101      -3  234  246      5   85   72     11   81   75     -2   99   92     -3  142  148      9   67   62
 15  101   90      -4   65   66      -1  156  140                      15   82   77      0   52  38*    -1  166  144
                    -2   57   53       3   47   46                                       4  157  148      1   85   83     H= 10 K=-10
 H=   5 K=-11      -5  186  175       5   97   90     H=   7 K=-13     H=   7 K= -1      6  143  149      5   65   66    -18   67   62
-12   97   82      -3  171  287*      7  136  133     -6   86   61    -16   89   93      8  160  153      7  114  110    -14   83   77
-10  100   93       3  219  217       9  160  164     -2   93   89    -14   82   90     10  144  147      9  128  130    -14   66   66
 -8   95   97       5  108  105      11  173  177      0   78   6R    -12   74   77     12   74   72     11  126  124    -12   68   59
 -6   91  101       9   88   82      13  115  125                     -8   83   74                      13   86   96     -6   63   52
 -4   81   70      11  114  120                       H=   7 K=-12    -6  114  108     H=   8 K= -3                      -4  136  137*
  2  102  105      13  156  139     H=   6 K= -6     -11  113  118     -4  158  149    -17   86   77     H=   9 K= -7    -2  166  159
  4  123  102      15  131  138     -16   73   65      -9  117  128     -2  179  206    -15  113  103      4   60   57      4   52   66
  6  109  126                      -14   96  100      -7  113  114      2  106  103    -13  112  119                     10   79   71
  8   88   94      H=   5 K= -9     -12   96   86      -5   91   79      6   54  41*    -11  111  88*     H=   9 K= -6    12   83   87
                  -12   83   91     -10  111  124      -1   80  56*     8   80   74     -5   87   95     -7   72   71     14   88   81
 H=   5 K= -9     -10  122  116     -R  126  121       3  141  125     10  119  101     -3  210  208     -5  100   92     16   78   73
-12   83   91      -8  162  147      -R  143  134       5  144  142     12  137  146     -1  247  218     -3  120  125     18   68   50*
-10  122  116      -6  236  219      -6   74   67       7  125  137     14  110  103      1  215  215     -1  141  137
 -8  162  147      -4  207  202      -2  205  183       9  100   95                      3  191  197      1   82   70     H= 10 K= -9
 -6  185  183       4  205  193      0  173  152                      H=   8 K=-17      5  128  132      7   82   87     -9   60   48
 -4  110  118       8  184  184      2  147  135     H=   7 K=-11     -3  101  81*      7   78   74      9  120  116     -7   73   62
 -2   90   89       R  179  175      4  171  171     -4   97   93     -1   93   93*    11  130  119     11   82   92     -5   49   49
  2  114  111      10  144  148      6  105  105     -4  111  108      3   94   88     13  128  121                      3   53   55
  6  148  158      12   61   69     14   70   77     -2   99   80                      15   98  108     H=   9 K= -5      5   60   66
  6  18R  207                       16   75   93      0  108  101     H=   8 K=-16     17   97   94    -14  104  116      7   76   84
  8  158  164      H=   6 K=-17                       2   92   90     -4   88   74                     -12  122  135*     9   68   68
 10   79   94      -7   81  100     H=   6 K= -5      4   73  55*                      H=   8 K= -2    -10  125  126
 12   71   71      -5  123  110     -3   39   41      8   79  60*     H=   8 K=-14     -6   66   72     -8  123  121     H= 10 K= -8
                  -3   86   88     -1   38   31     10   99   95     -8  105  100     -4   71   44     -6   90   86     -4   64   53
 H=   5 K= -8      5   80   63*                     12  105   95     -6  101   98     -2   77   70     -4   42   39     -2   76   69
-17   97   93      7   R2   86     H=   6 K= -4                       -4   99   90      0   58   60     -2   92   89      0   52   52
-15   98  105                      -14  110  105     H=   7 K= -9     -4   86   76      2   37   26*    0  154  148      2   67   47
-13   91   97      H=   6 K=-1R    -12  100  107     -4  142  145     -6  112  117      4   60  46*     2  183  191      4   47   43
-11   85   82     -2   75   55*    -10  136  127    -10  136  127     -8  116  115      8   98   8R     4  217  216
 -5  135 105*      0   81   76     -R  128  119     -2  132  150     10   93   85      R   75   76     6  188  169     H= 10 K= -7
 -3  225  213      2   75   8R     -6   66   69      0  155  143                                       8  111  104    -13   64   61
 -1  273  255      4   77   67     -4   71   5R                      H=   8 K=-13     H=   8 K= -1     16   98   89    -11   93   90
  1  241  228                      -2  189  165     H=   7 K= -8     -3   93   89    -13   78   80                      -9  155  140
  3  165  159      H=   6 K=-14     0  221  163*   -13   88   85     -1  110  116    -11   83   80     H=   9 K= -4     -7  171  151
  5   54   52    -12   80   86      2  206  210    -11  107· 120      1 ·110  128     -5   58   61     -9   62   51     -5  127  106
 11   94  103    -10  100   93      4  218  221     -9  136  141      3  103  108     -3  125  121     -7   87   83     -3   56   64
 13  141  133     -2   89   84      6  130  125     -7  159  146      5   82   81      1  123  150     -5  109   99      1   84   90
 15   92 121*     0  133  13R      R  117   99     -5  126  101                       3  123  133     -5  117  100      3   90  106
 17   83   79     2  147 ·144     12   R0   72      1  113  119     H=   8 K=-11     5  120  110     5   90   74     5  144  143
                  4  132  118     14   95   94      3  180  183     -1   83   90    11   74   74     8   93   74*    7  142  158
 H=   5 K= -7     6   73   77     16   73   96*     5  219  220     1  108  112    13   75   88     7   78   74     9  168  122
-10   61   43*                                       7  194  173     3  121  104                     11   86   90    11   57   62
 -8   61   44*     H=   6 K=-13    H=   6 K= -3      9   94  102     5   75   67    H=   8 K=  0     13   79   75
 -4   69   66     -9   73   75    -21   84   73                                     -18   R8   82                     H= 10 K= -6
  0   46   38     -7.  108· 113   -19   R5   75                      H=   8 K=-10    -12   80   79    H=   9 K= -3    -16   77   60
  2   73   59     -5  140· 141    -17   73   66     H=   7 K= -6     -8  101  111    -10  159  166    -2   47.  55    -16   78   71
  6   50   60     -3  125  138    -15   67   73    -15   77   65    -10  101  111     -8  196  216     0   80   73    -12   66   57
                  -1  100  105    -13   56   37*   -11·  92   95     -6  138  166     -6  197  179     2   88   80    -10   51   49
 H=   5 K= -6      5   6R   79    -11   72   85     -9  121  116     -4  139  136     -4  139  141     6   73   62     -6   77   67
-17   78   67      7  119  111    -9  187  16R*    -7  111   99     -2   79   80     -2  102  130*    8   51   45     -4  105   92
-15   73   77      9  113  109    -7  241  250     -5   84   74*     0   60   45*    -2  102  130*                    -2  152  105*
-13   95   88     11   77  103*   -5  329  308     -3   56  41*      4   93   69*     4   76   70    H=   9 K= -2     0  164  154
-11   87   74                     -3  2R3  270     -1   93   69*    6  135  137     6  198  200    -9   94   85     2  123  129
 -5   88   74     H=   6 K=-11    -1  191  174     1  106   91     8  142  151     8  198  195    -7  156  156     4   71   73
 -3  212  202     -7  107  108     1   63   58     3  132  130    10  114  128    10  136  144    -5  237  211    10   58   61
 -1  188  198     -5  127· 130     R   91   81     5  149  151                    12   92  105    -3  204  202    12   90   86
  1  199  166     -3  133   96*    R  110  10R     7  137  125                                    -1  178  197    14   97   90
  3  109  104     -1   76   68     7  173  18?     9   67   71     H=   8 K= -9                     1  120  129    16   67   65
 11   82   88      1   59   51     9  223  237                     -3   82   76    H=   9 K=-16    3  146  132
 13   97  106      5   81   75    11  16R  190    H=   7 K= -5     -1   80   81    -5   78   73    7  142  143    H= 10 K= -5
 15   97  100      7   91  100    13   98  113    -14  103  100     1   81   87    -3   77   86    9  136  146    -7   55   55
                   9   81   R7                     -12   86   90    3   91   85                   11  143  141
 H=   5 K= -5     11   72   87    H=   6 K= -2      -8   77   75                   H=   9 K=-15    13  109  117    H= 10 K= -4
-12  106  121                     -R   46   40     -6  142  161    H=   R K= -?    -3   73   77    15   84   73    -18   73   67
-14  157  179     H=   6 K=-10     -6   51   61     -4  203  221    -8   68   60     2  124  114                    -16   74   86
  8  184  188    -14   97   98     -6   69   66     -2  237  248    -6   60   79     R   97 125*   H=   9 K= -1    -14   75   79
 -6  148  156    -12  118  127     -2   40  56*     0  204  205    -4   60   59     6  100   92   -14   83   89    -12   63   51
 -4  175  179    -10  101  107     2   44   47     2  162  159    -6   85   77                   -12  119  129     -6   92  70*
 -2  104   99    -R   96   94     4   78   65     4   60   55     8   70   67    H=   9 K=-13    -10  111  125    -14  110  124
  0   82  60*    -4   57   67                     8   94   89                     2   73   70    -8  133  120    -2 ·190  176
  2  148  151    -2  118  103    H=   6 K= -1     6  166  164    H=   8 K= -7     4   69   72    -6   80   71     0  165  152
  4  259  241     0  194  149   -11   54   65    12  146  149   -15  102  106                    0   70  103*    0  127  152
  6  171  196     2  197  193    -9   91   90    14  116  118   -13  102  104    H=   9 K=-12    2  133  148     2  160  150
  8  190  208     6  146  157    -7  144  133                   -11   94  110   -7   81   89     4  143  179     6   83   78
 10  149  157     6  12R  146    -5  133  117    H=   7 K= -4    -9   73   65   -5  124  125     6  194  204    10   88   79
 12   77   78     R   9R  78*    -3  110  164*  -11   96  101    -7   75   43   -3  132  136     8   64   68    12  101   98
                 12   72   66    7  11R  133    -9  135  124    -5  103  100   -1  120  122                    14   94   90
 H=   5 K= -4    14   76   95    9  138  151    -7  148  145    -1  209  204                    H= 10 K=-11    16  101   81
-15   84   88                   11  110  128    -5   74   64    3  208  235     7   66   68    -9   67   68
-13   77   83    H=   6 K= -0   13   96   89    -3   51   45    5  239  232     7   90   87    -7   71   66    H= 10 K= -3
-11   58   55    -9   61   53                   -1   75   61    5  145  139    11   83   97    -5   64   62    -13   71   66
```

Table 4. Continued.

[Table of observed and calculated structure factors — dense multi-column numerical data, grouped by h, k index blocks.]

The final atomic parameters are given in Table 3 and the observed structure factors are compared with those calculated in the last cycle of refinement in Table 4. The electron density maps of a difference synthesis based on the parameters in Table 3 showed only spurious peaks, all less than 2 $e/Å^3$.

All computations were performed on the UNIVAC 1108 computer at Lund, Sweden, using the programmes DRF, LALS, DISTAN, PLANE, CELSIUS, and ORTEP.[7]

DESCRIPTION OF THE STRUCTURE

The structures of NDH and NDO are closely related. In the following description the structure of NDH is mainly compared to that of NDO which

was reported in Ref. 1. References to other related structures were given in that paper. The notation of the atoms is the same as that used in Ref. 1, and the superscripts $(i)-(x)$ indicate the following equivalent positions of the structure,

	x,y,z	(iv)	$1/2+x,1/2-y,z$	(viii)	$x,\bar{y},z-1/2$
(i)	$\bar{x},\bar{y},\bar{z}$	(v)	$x-1/2,1/2-y,z$	(ix)	$x,\bar{y},1/2+z$
(ii)	$\bar{x},y,1/2-z$	(vi)	$1/2-x,1/2+y,\bar{z}$	(x)	$1/2-x,y-1/2,\bar{z}$
(iii)	$1-x,\bar{y},\bar{z}$	(vii)	$1/2-x,1/2-y,1/2-z$		

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

The general features of the structure are shown in Figs. 1 and 2. The neodymium ions are held together in pairs by oxygen bridges formed by the carboxylate oxygen O(2) of ligand 1 (Fig. 1). These pairs are situated at
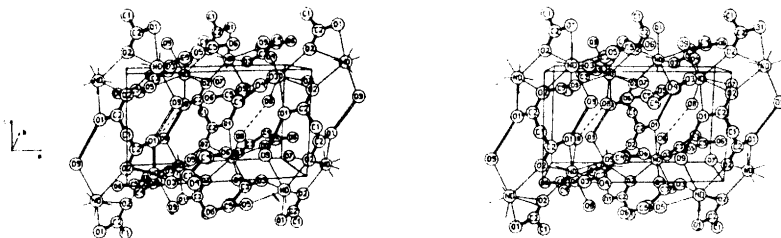
Fig. 1. A stereoscopic pair of drawings showing part of two adjacent neodymium malonate networks and the bonding between them. Bonds within the malonate ions are filled, hydrogen bonds are open and Nd−O bonds are single lines. The broken line indicates the possible hydrogen bond distance O(8)−O(8^{vii}). The intra-network hydrogen bonds are omitted for clarity. The box outlined is $0 \leq x \leq 1$, $0 \leq y \leq 1/2$, $0 \leq z \leq 1/2$.
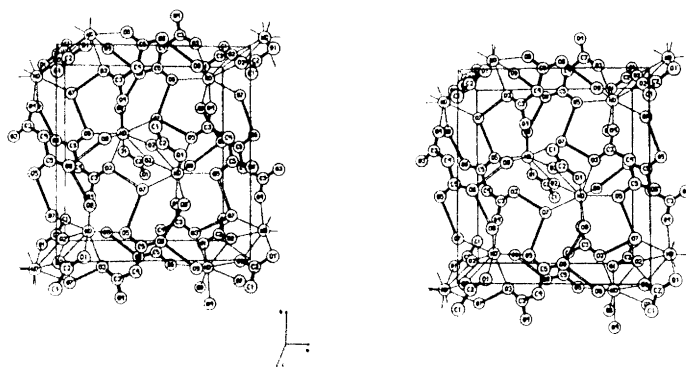
Fig. 2. A stereoscopic pair of drawings illustrating the neodymium malonate network around $z=0$. The bonds are indicated in the same way as in Fig. 1. The box outlined is $0 \leq x \leq 1$, $0 \leq y \leq 1$, $-1/4 \leq z \leq 1/4$.

the levels $z = 0$ and $z = 1/2$. The methylene carbon of ligand 1, C(1), is situated on the twofold axis $x = 0$, $z = 1/4$ and ligand 1 thus connects the neodymium pairs in the z-direction.

Within the same z-level, each neodymium pair is bonded to four adjacent pairs by bridges of the type Nd−OCO−Nd, formed by ligand 2 (Fig. 2). In this way infinite neodymium-malonate networks parallel with (001) are formed.

The structure of NDO contains corresponding neodymium pairs bonded to each other in a similar manner, but while adjacent pairs at the same z-level are related by the a-glide in NDH, they are related by the b-glide in NDO.

The three water molecules are all coordinated to neodymium. They form hydrogen bonds to the oxygens of ligand 2 within the neodymium malonate network (Fig. 2) and one of them, O(9), is also hydrogen bonded to a carboxylate oxygen, O(1), of an adjacent network (Fig. 1). The intra-network hydrogen bonds are arranged in almost the same way as found in NDO, but corresponding distances between hydrogen bonded oxygens are about 0.1 Å longer in NDH than in NDO. The inter-network hydrogen bonds, which in NDH are formed directly between a water molecule of one network and a carboxylate oxygen of an adjacent one, are in NDO formed via a water molecule located between the networks. This is the essential difference between the two hydrogen bond systems, and results in a decrease in the distance between adjacent networks as indicated by the change in length of the c-axis from 14.69 Å in NDO to 13.69 Å in NDH.

The coordination polyhedron. Fig. 3 shows the coordination around the pair of neodymium ions. There are nine oxygens coordinated to each neo-
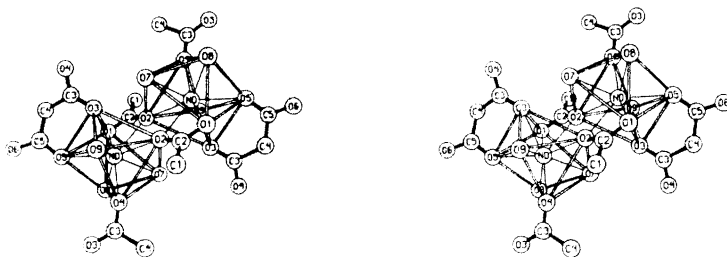
Fig. 3. A stereoscopic pair of drawings showing the coordination polyhedra around the neodymium ions Nd and Nd^i. Nd−O bonds are single lines, the bonds within the malonate ions are filled and the edges of the square antiprism are open.

dymium, six carboxylate oxygens from four malonate ions and three water oxygens. The coordination polyhedron is an intermediate between a mono-capped square antiprism (CSAP) and a tricapped trigonal prism (TCTP). The "square" faces of the CSAP are O(1)−O(7)−O(2^i)−O(3) and O(4^{vi})−O(9)−O(5)−O(8) and the TCTP has the triangular faces O(1)−O(3)−O(5) and O(2^i)−O(7)−O(4^{vi}). There is a close relationship between the idealized forms

of TCTP and CSAP [8] and with the rather irregular polyhedron dealt with here, the choice of description seems to be a matter of semantics. The CSAP model is chosen in order to facilitate a comparison with the distorted CSAP formed around neodymium in NDO. The dimensions of the coordination polyhedron are given in Table 5 A.

The average Nd – O bond distance is 2.50 Å; the same value as found in NDO. Two of the distances deviate considerably from this average, viz. Nd – O(4^{vi}): 2.35 Å, and Nd – O(2): 2.61 Å, while the others are in the range 2.41 – 2.56 Å. The bond Nd – O(2) is part of the oxygen bridge Nd···O(2)···Nd^i. The distance O(2) – Nd^i is 2.47 Å and Nd···Nd^i is 4.33 Å. This bridge is less asymmetric in NDH than in NDO where the corresponding distances are 2.72 Å, 2.46 Å, and 4.42 Å. The distance Nd···Nd^i is the shortest Nd···Nd distance of the structure. The next shortest one, 6.58 Å, is between the neodymium ions Nd and Nd^{vi} coupled by the bridging carboxylate group O(3)C(3)O(4).

The average "contact" distance between coordinated oxygens not belonging to the same malonate ion is 2.96 Å as compared to 3.00 Å in NDO. Two of these distances are shorter than 2.8 Å, viz. O(2)···O(2^i): 2.66 Å and O(3)···O(9): 2.79 Å.

The coordination around Nd is very similar in NDH and NDO (see Fig. 3 in Ref. 1 and Fig. 3). Apart from the fact that the oxygens O(8) and O(4^{vi}) change places between the two structures there are only minor rearrangements. The coordination polyhedron in NDO is best described as a distorted CSAP. The slight distortions that occur in going from NDO to NDH bring the polyhedron closer to the TCTP model. This change of the polyhedron may be described as follows: The quadrangle O(1) – O(7) – O(2^i) – O(3) is equilateral within 0.1 Å in NDO. In NDH it is approximately rectangular with the edges 3.48 Å, 2.87 Å, 3.36 Å, and 2.85 Å. In both structures the four atoms are coplanar within 0.2 Å. The other quadrangle, formed by the oxygens O(4^{vi}), O(9), O(5), and O(8) is equilateral within 0.1 Å in both structures. The four atoms are coplanar within 0.1 Å in NDO. In NDH they deviate ± 0.3 Å from the least squares plane through them, in the directions expected in a TCTP. Further, the bond distance between neodymium and the capping oxygen O(2) is in NDO 2.72 Å, i.e. considerably longer than the other Nd – O bond distances. This feature is less pronounced in NDH where the distance Nd – O(2) is 2.61 Å.

Ligand 2 forms a six-membered chelate ring with neodymium. The ring has a boat conformation. The atoms O(3), C(3), C(5), and O(5) are coplanar within 0.06 Å and the atoms Nd and C(4) are situated 0.32 and 0.44 Å at the same side of the plane (Table 6). The corresponding values in NDO are 0.42 and 0.50 Å, and hence the changes in its crystallographic surroundings result in a flattening of the ring in going from NDO to NDH.

The malonate ions. The dimensions of the two independent malonate ions are given in Table 5 and are also indicated in Fig. 4. The bond distances and angles are in agreement with those found in NDO, with two exceptions, viz. the angle C(2) – C(1) – C(2^{ii}) which is 104° in NDH and 113° in NDO and the angle C(4) – C(3) – O(4) which is 112° in NDH and 120° in NDO.
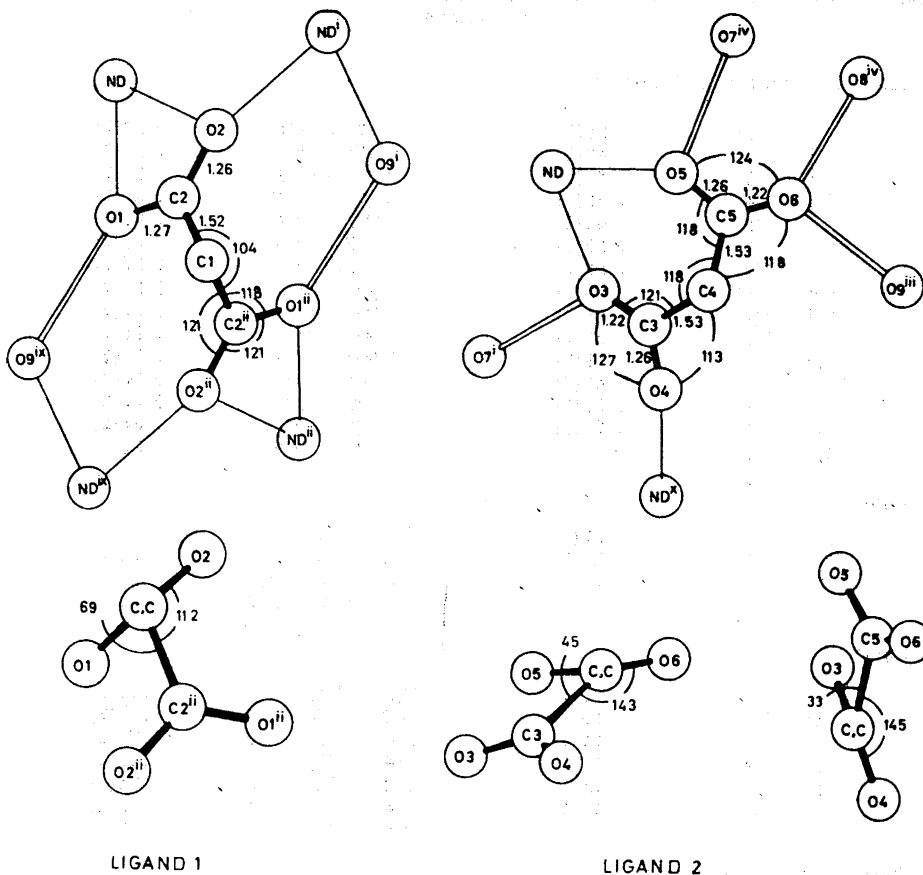
Fig. 4. The two malonate ions and their immediate surroundings, together with projections of each malonate ion along its C – C bonds. The angles indicated in these projections are the dihedral angles C – C – C – O.

The three independent C – COO groups are planar (Table 6). The methylene carbon C(1) of ligand 1 is situated on a twofold axis and the dihedral angle C(2^{ii}) – C(1) – C(2) – O(1) is 69°, which means that the two COO-groups are twisted through this angle in opposite directions out of the carbon chain plane. The resulting intramolecular separations between oxygens of different COO-groups are O(1)···O(2^i): 3.42 Å and O(1)···O(1^{ii}): 3.51 Å. In NDO the corresponding twist is 50° and the O – O distances are O(1) – O(2): 3.78 Å and O(1) – O(1^{ii}): 3.24 Å.

In ligand 2, the dihedral angles O(3) – C(3) – C(4) – C(5) and O(5) – C(5) – C(4) – C(3) are 33° and 45°, respectively, and the carboxylate groups are twisted in the same direction out of the plane of the three carbon atoms. The shortest intramolecular separation between oxygens of different car-

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

A. The coordination polyhedron

Nd – O(1)	2.56(1)	O(2^i) – O(4^{vi})	3.37(2)
Nd – O(2^i)	2.47(1)	O(2^i) – O(7)	2.87(2)
Nd – O(3)	2.45(1)	O(2^i) – O(9)	2.97(2)
Nd – O(4^{vi})	2.35(1)	O(2^i) – O(2)	2.66(2)
Nd – O(5)	2.41(1)	O(3) – O(5)	2.80(2)
Nd – O(7)	2.53(1)	O(3) – O(9)	2.79(2)
Nd – O(8)	2.55(2)	O(3) – O(2)	2.87(2)
Nd – O(9)	2.55(1)	O(4^{vi}) – O(5)	3.51(2)
Nd – O(2)	2.61(1)	O(4^{vi}) – O(7)	3.07(2)
O(1) – O(3)	2.88(2)	O(4^{vi}) – O(8)	2.96(2)
O(1) – O(5)	3.19(2)	O(4^{vi}) – O(9)	2.90(2)
O(1) – O(7)	3.47(2)	O(5) – O(8)	3.00(2)
O(1) – O(8)	3.03(2)	O(5) – O(9)	3.12(2)
O(1) – O(2)	2.20(1)	O(7) – O(8)	2.84(2)
O(2^i) – O(3)	3.36(1)	O(7) – O(2)	2.86(2)

B. Ligand 1

C(1) – C(2)	1.52(2)	C(2) – C(1) – C(2^{ii})	104(2)
C(2) – O(1)	1.27(2)	O(1) – C(2) – O(2)	121(1)
C(2) – O(2)	1.26(2)	C(1) – C(2) – O(1)	118(1)
		C(1) – C(2) – O(2)	121(1)

C. Ligand 2

C(4) – C(3)	1.53(2)	C(3) – C(4) – C(5)	118(1)
C(4) – C(5)	1.53(2)	O(3) – C(3) – O(4)	127(2)
C(3) – O(3)	1.22(2)	C(4) – C(3) – O(3)	121(1)
C(3) – O(4)	1.26(2)	C(4) – C(3) – O(4)	113(1)
C(5) – O(5)	1.26(2)	O(5) – C(5) – O(6)	124(1)
C(5) – O(6)	1.22(2)	C(4) – C(5) – O(5)	118(1)
		C(4) – C(5) – O(6)	118(1)

D. Possible hydrogen bonds

O(7) – O(3^i)	2.74(2)	O(8) – O(8^{vii})	2.83(2)
O(7) – O(5^v)	2.84(2)	O(9) – O(6^{iii})	2.72(2)
O(8) – O(6^v)	2.74(2)	O(9) – O(1^{viii})	2.85(2)

boxylate groups, the ligand bite O(3) – O(5), is 2.80 Å. This conformation is slightly different from that found for ligand 2 in NDO where the twists are 42° and 48° and the bite 2.83 Å.

The hydrogen bonds. The distances suitable for hydrogen bond formation, *i.e.* the distances (H$_2$)O – O between oxygens not belonging to the same coordination polyhedron [9] shorter than 3.20 Å, are collected in Table 5. They are also indicated in Fig. 5 which illustrates a probable hydrogen bond scheme.

The water molecule O(7) forms two hydrogen bonds, each to a car-boxylate oxygen within the neodymium-malonate network, *viz.* O(7)···O(3^i) and O(7)···O(5^v). The water molecule O(9) also forms two hydrogen bonds, one

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

A. The malonate ions

Atom	Distance	Atom	Distance	Atom	Distance	Atom	Distance
C(1)	0.00	C(4)	0.00	C(4)	−0.01	C(3)	−0.06
C(2)	−0.00	C(3)	−0.01	C(5)	0.04	C(5)	0.06
O(1)	0.00	O(3)	0.00	O(5)	−0.01	O(3)	0.06
O(2)	0.00	O(4)	0.00	O(6)	−0.02	O(5)	−0.05
*		*		*		*	
Nd	−0.07	Nd	−0.14	Nd	0.36	Nd	−0.32
Nd^i	0.10	Nd^x	0.55			C(4)	−0.44

B. The coordination polyhedron

Atom	Distance	Atom	Distance
O(3)	−0.23	O(8)	0.31
O(1)	0.22	O(4^{vi})	−0.33
O(7)	−0.22	O(5)	−0.28
O(2^i)	0.23	O(9)	0.30
*		*	
Nd	−1.16	Nd	1.30

to the carboxylate oxygen O(6^{iii}) within the neodymium malonate network and the other to the carboxylate oxygen O(1^{viii}) of an adjacent network.

The hydrogen bond situation of the water molecule O(8) is less evident. One of its hydrogen atoms is engaged in an intra-network hydrogen bond to the carboxylate oxygen O(6^v). The position of the second hydrogen atom
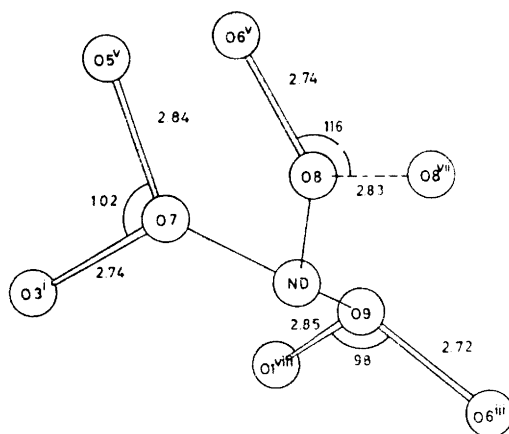
Fig. 5. The immediate surroundings of the three water molecules. Hydrogen bonds are open and Nd−O bonds are single lines. The possible bond O(8)−O(8^{vii}) is indicated by the broken line.

is more difficult to establish. The distance $O(8)\cdots O(8^{vii})$ is 2.83 Å indicating a hydrogen bond. This interpretation implies a disordered structure in which the center of symmetry between $O(8)$ and $O(8^{vii})$ is preserved by randomly assigning the shared hydrogen atom to one oxygen or the other. The next shortest $O(8) - O$ distance outside the coordination polyhedron is $O(8)\cdots O(3^{vi})$, 3.56 Å. If a hydrogen bond interaction $O(8)\cdots O(8^{vii})$ exists, it constitutes an additional inter-network link.

Assuming a hydrogen bond $O(8)\cdots O(8^{vii})$ each water oxygen is engaged in three bonds, one to neodymium and two hydrogen bonds. The sum of the three bond angles is 352° around $O(7)$, 359° around $O(8)$, and 341° around $O(9)$. The $O - O(W) - O$ donor angles are given in Fig. 5.

There are thus four intra-network hydrogen bonds in NDH, viz. $O(7)\cdots O(3^{i})$, $O(7)\cdots O(5'')$, $O(8)\cdots O(6'')$, and $O(9)\cdots O(6^{iii})$. Corresponding hydrogen bonds are formed in NDO. In the latter structure they are about 0.1 Å shorter than in NDH except for the bond $O(9)\cdots O(6^{iii})$ which is of equal length in the two structures. As mentioned earlier, the inter-network hydrogen bonds of NDO are formed via a water molecule situated between the networks. The insertion of this extra water molecule in the structure results in a hydrogen bond system where each of the water hydrogen atoms is engaged in a separate bond. These features probably contribute to making the lattice energy less for NDO than for NDH.

The hydrogen bond $O(1^{ii})\cdots O(9^{i})$ is of some interest. It is seen in Fig. 4 that ligand 1 may be regarded as chelated to neodymium via this hydrogen bond to one of the coordinated water molecules. The existence of chelates of this type has been suggested for the lanthanoid glycolate complexes in solution. Both thermodynamic [10] and IR [11] data have been interpreted in this way. A thermodynamic study of the formation of lanthanoid malonate complexes in solution shows that the complexes formed are fairly weak for a chelate. Furthermore, the variation through the lanthanoid series in ΔH_{j}° and ΔS_{j}° deviates from that ordinarily found for lanthanoid chelates. This deviation might be explained if species with the malonate ion chelated via a water ligand of the metal ion are formed in increasing amounts through the series.[12] The existence of a corresponding chelate in the solid state supports this idea.

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