ACTA CHEMICA SCANDINAVICA 27 (1973) 2441–2454

Structural Studies on the Rare Earth Carboxylates

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

EVA HANSSON

Physical Chemistry 1, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund 7, Sweden

The crystal and molecular structure of $Nd_2(C_3H_2O_4)_3.8H_2O$ has been determined from three-dimensional, photographic, X-ray intensity data. The crystals are orthorhombic with $a = 11.258(3)$ Å, $b = 12.602(3)$ Å, and $c = 14.689(3)$ Å. $Z = 4$. The space group is *Pbcn*. The structure is a three-dimensional neodymium-malonate network. Each neodymium ion is coordinated by six carboxylate and three water oxygens which form a monocapped square antiprism. The Nd – O bonds are in the range 2.41 – 2.72 Å. There are two independent malonate ions in the structure. They are both nonplanar. One of them has strict twofold symmetry and is bonded to four neodymium ions by six Nd – O bonds, *i.e.* two of its oxygens form two Nd – O bonds each. The other malonate ion forms a six-membered chelate ring with neodymium and one bridge of the type Nd – OCO – Nd. The chelate ring has boat conformation. The water molecules are hydrogen bonded with O – O distances in the range 2.63 – 2.85 Å.

Thermodynamic studies of the lanthanoid oxalate and malonate complexes formed in solution [1,2] show that the five-membered chelate ring of the oxalate complexes is more stable than the six-membered ring of the malonate complexes. Further a maximum of four oxalate groups are coordinated to the lanthanoids while the corresponding number of malonate groups is three. Knowledge of the structures of some related solid compounds would facilitate the understanding of these differences.

The structures of some lanthanoid oxalates, $M_2ox_3.nH_2O$ (M = lanthanoid, $ox = C_2O_4^{2-}$) have been reported previously.[3,4,5] The oxalate ions form planar five-membered chelate rings with the lanthanoids with a ligand bite, *i.e.* intra-ring distance between the two donor atoms, of about 2.65 Å.

The ligand bite of the malonate ion depends on its conformation and with normal bond distances and angles it may range from about 2.5 Å for a completely planar ion to about 3.5 Å when the carboxylate groups are twisted 90° out of the plane of the three carbon atoms. The only X-ray study of coor-

dinated malonate ions previously reported deals with malonate complexes of Co(III) and Cr(III).[6] The malonate ions in these complexes form six-membered chelate rings and are nonplanar with bites larger than 2.65 Å.

The compounds $M_2mal_3.nH_2O$ ($mal = CH_2(COO)_2^{2-}$) were chosen for a X-ray structure analysis in order to determine the conformation of the malonate ion when coordinated to the lanthanoids and to study the resulting coordination geometry around the lanthanoid ion. Azikov *et al.*[7] have studied the IR-spectra of these solids. Their interpretation of the spectra indicates the presence of six-membered chelate rings in the complexes.

The lanthanoid malonates, $M_2mal_3.nH_2O$, can be divided into three different isostructural groups; one with $n = 8$ and M = Ce – Gd (referred to as octahydrate type I below), another with $n = 6$ and M = Ce – Eu, and a third type with $n = 8$ and M = Eu – Lu (octahydrate type II). This paper deals with the structure of $Nd_2(CH_2(COO)_2)_3.8H_2O$ (NDO). The two other structure types will be reported in following communications.

EXPERIMENTAL

Preparation. The lanthanoid malonates, $M_2mal_3.nH_2O$, were precipitated from solutions of the various lanthanoid chlorides (10 mM) and malonic acid (15 mM) with the pH adjusted to about 5 by the addition of 0.1 M sodium hydroxide. Slow evaporation at room temperature resulted in the octahydrate type I for the elements Ce – Gd and the octahydrate type II for the elements Tb – Lu. The octahydrate type II with M = Eu and Gd were obtained by evaporation under a heating lamp. The hexahydrates with M = Ce – Eu form at low temperature (5°C) but also by chance at higher temperatures, *e.g.* $Nd_2mal_3.6H_2O$ has been obtained at 70°C.

The compounds $Nd_2mal_3.8H_2O$ (type I), $Nd_2mal_3.6H_2O$, and $Eu_2mal_3.8H_2O$ (type II) were analysed for M, C, and H with the following results (%):

		M	C	H
$Nd_2mal_3.8H_2O$	Found	39.1	14.6	3.2
	Calc.	39.0	14.6	3.0
$Nd_2mal_3.6H_2O$	Found	41.1	15.1	2.6
	Calc.	40.9	15.3	2.6
$Eu_2mal_3.8H_2O$	Found	40.5	14.9	3.2
	Calc.	40.2	14.3	2.9

The different phases of the other lanthanoid malonates were then identified by their X-ray powder patterns. When precipitated from the solutions described the crystals of the various phases are also easily recognized by their habits. The crystals of the octahydrates are orthorhombic; thick tabular (001) bounded by the faces {001}, {010}, and {110} for type I and acicular elongated *b* for type II, while the hexahydrate crystals are monoclinic and thick tabular (001) bounded by the faces {001}, {010}, and {100}.

All the hexahydrates and the octahydrates type II with M = Eu and Gd are transformed to octahydrate type I when stored in the mother liquor at room temperature for a long time (sometimes more than two years). Thus the octahydrate type I is the stable phase for M = Ce – Gd under these conditions.

X-Ray diffraction work. A crystal of the dimensions $0.22 \times 0.13 \times 0.13$ mm³ mounted along the 0.22 mm edge was used in recording the layers $0kl - 14kl$, with the integrated, Weissenberg, multi-film technique. Zr-filtered Mo-radiation was used. The intensities of 1876 independent reflexions were measured visually by comparison with a calibrated scale. 1390 of these reflexions were within the copper sphere representing 53 % of the possible number.

The intensities were corrected for the Lorentz, polarisation and absorption effects. The linear absorption coefficient, μ, is 50 cm^{-1} and the transmission factors, evaluated by numerical integration, were in the interval 0.54 – 0.61.

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

The crystals of NDO are orthorhombic with $a = 11.258(3)$ Å, $b = 12.602(3)$ Å, and $c = 14.689(3)$ Å and $Z = 4$. The accurate values of the cell parameters were determined from powder data by least squares refinement, as described in Ref. 5. The observed values of $\sin^2\theta$ are compared with those calculated in the last cycle of refinement in Table 1.

Table 1. Powder data for $Nd_2(C_3H_2O_4)_3.8H_2O$. 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 1 0	847	843	s	1 4 2	7576	7558	w
0 0 2	1101	1102	vs	2 4 0	7861	7863	w
1 1 1		1119		4 1 1	8161	8152	m
0 2 0	1499	1497	w	3 2 3		8196	
2 0 0	1880	1876	w	4 0 2	8609	8604	w
1 1 2	1948	1945	m	3 3 2	8687	8690	vw
1 2 1	2237	2241	vs	1 2 5	8885	8853	m
2 1 1	2523	2525	s	2 4 2	8990	8965	m
2 0 2	2972	2978	w	4 2 0		8999	
1 2 2	3063	3068	vvw	2 1 5	9118	9137	vvw
2 2 0	3370	3372	w	0 0 6	9923	9918	vw
2 2 1	3645	3648	w	4 1 3		10356	
0 0 4	4446	4408	s	1 0 6	10384	10387	m
1 2 3		4445		0 4 4		10395	
2 2 2	4595	4594	w	1 1 6	10770	10761	w
2 1 3	4732	4729	m	4 0 4	11888	11910	vw
1 0 4	4868	4877	w	3 3 4	11992	11996	vw
1 3 2	4930	4939	w	2 3 5	12121	12131	s
1 1 4	5246	5251	s	3 2 5	12607	12604	vw
2 3 1	5514	5519	s	0 6 0		13471	
3 1 2	5699	5696	s	4 4 0	13487	13490	s
2 2 3	5846	5852	vw	5 2 1		13495	
0 4 0	5994	5987	m	3 5 0	13572	13575	w
3 2 1		5992		2 5 3	13719	13710	vw
1 4 1	6731	6732	vw	1 3 6		13755	
3 2 2	6816	6819	vw	1 6 1	14210	14216	m
0 4 2	7082	7089	s	1 5 4		14232	
4 0 0	7510	7502	w				

Weissenberg photographs show the systematic absences $0kl$: $k \neq 2n$, $h0l$: $l \neq 2n$ and $hk0$: $h + k \neq 2n$ and thus the only possible space group is $Pbcn$ (No. 60).[8]

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The structure was determined by the heavy atom method. The position of neodymium was obtained from a three-dimensional Patterson synthesis and a subsequent difference electron density calculation revealed the positions of the remaining 15 non-hydrogen atoms.

The preliminary atomic coordinates and isotropic temperature factors together with the inter layer scale factors were improved by full-matrix least squares refinement. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with

Table 2. Analysis of the weighting scheme $w = 1/(40 + |F_o| + 0.005|F_o|^2 + 0.0001\ |F_o|^3)$. 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 – 40	155	0.84	0.00 – 0.28	322	0.94
40 – 46	174	0.96	0.28 – 0.35	289	0.98
46 – 49	171	0.97	0.35 – 0.40	242	0.90
49 – 54	176	0.96	0.40 – 0.44	201	0.94
54 – 61	177	1.08	0.44 – 0.48	188	0.97
61 – 71	179	0.95	0.48 – 0.51	166	0.98
71 – 85	184	0.99	0.51 – 0.53	108	0.95
85 – 103	181	0.97	0.53 – 0.56	74	0.77
103 – 140	182	1.09	0.56 – 0.58	59	1.41
140 – 423	171	1.19	0.58 – 0.60	40	1.17

Table 3. Atomic parameters with estimated standard deviations for the compound $Nd_2(H_2C_3O_4)_3.8H_2O$.

Atom	Group	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	B/Å^2
Nd		1491.7(6)	1134.3(5)	74.1(3)	(1.37)[a]
O(1)	COO^-	1038(12)	850(10)	1750(8)	2.8(2)
O(2)	COO^-	−167(9)	−88(8)	911(7)	2.1(2)
O(3)	COO^-	2199(10)	−697(9)	307(7)	2.4(2)
O(4)	COO^-	3147(12)	−2155(11)	752(8)	3.1(2)
O(5)	COO^-	3545(11)	1162(9)	604(7)	2.7(2)
O(6)	COO^-	5343(15)	711(13)	952(10)	4.1(3)
O(7)	H_2O	−515(10)	2028(9)	188(6)	2.4(2)
O(8)	H_2O	1368(16)	2403(11)	−1195(9)	3.7(2)
O(9)	H_2O	2780(12)	662(10)	−1242(8)	2.9(2)
O(10)	H_2O	3551(17)	2565(10)	−1958(10)	4.3(3)
C(1)		0	−527(18)	1/4	2.2(3)
C(2)		325(13)	131(11)	1675(9)	2.0(2)
C(3)		3032(12)	−1160(12)	764(8)	1.8(2)
C(4)		3855(18)	−494(16)	1362(13)	3.3(3)
C(5)		4295(17)	546(15)	966(11)	2.8(3)

[a] The anisotropic thermal parameters for neodymium, calculated from the expression: $\exp -(h^2\beta_{11} + 2hk\beta_{12} + ...)$ are $\beta_{11} = 0.00269(6)$, $\beta_{22} = 0.00186(5)$, $\beta_{33} = 0.00185(3)$, $\beta_{12} = 0.00007(4)$, $\beta_{13} = 0.00005(2)$, and $\beta_{23} = -0.00000(2)$, resulting in root mean square displacements along the principal axis of the thermal ellipsoid $R_1 = 0.142$ (Å), $R_2 = 0.122$ (Å), and $R_3 = 0.132$ (Å).

Table 4. Observed and calculated structure factors in $Nd_2(C_3H_2O_4)_3.8H_2O$. In each group the running index l, $|F_o|$, and $|F_c|$ are given. The 126 reflexions not obeying the condition $0.80 \leq |F_o|/|F_c| \leq 1.25$ are denoted by asterisks.

H=-14 K= 0
2 63 1164
4 81 109*
6 81 84
8 90 93
10 78 75
12 56 53
14 47 49

H=-14 K= 1
1 21 41*
3 33 48*
5 44 51
7 39 44
9 40 35

H=-14 K= 2
2 21 27*
9 35 29
11 34 33
15 45 39

H=-14 K= 3
1 30 47*
3 37 48*
5 46 50
7 41 44
9 38 40
11 39 37

H=-14 K= 4
0 89 104
2 87 105
4 82 95
6 87 88
8 69 73
10 59 61
12 64 60
14 53 50
16 48 36*

H=-14 K= 5
1 30 28

H=-14 K= 6
0 58 53
2 47 43
4 42 40
6 45 38
8 40 36
9 42 34

H=-14 K= 7
1 42 47
3 48 51
5 50 54
7 53 52
9 48 41

H=-14 K= 8
0 76 74
2 71 75
4 70 68
6 54 63
8 48 54
10 55 53
12 45 42

H=-14 K= 10
0 47 44
2 56 56
4 49 52
6 50 46
8 48 42
10 46 36*

H=-14 K= 11
1 50 50
3 46 46
5 47 46
7 53 46

H=-14 K= 12
0 48 47
2 48 41
4 49 42

H=-14 K= 14
0 57 55
2 57 51
4 52 49
6 53 45

H=-13 K= 1
0 48 103*
2 63 107*
4 71 102*
6 61 77*
8 80 84
10 64 68
11 39 38
12 48 58
14 57 51
16 48 36*

H=-13 K= 2
1 29 50*
3 35 49*
5 29 37*
7 40 41
9 42 42
11 33 29

H=-13 K= 3
0 51 74*
2 47 67*
4 52 59
6 54 62
8 44 48
9 46 38
10 45 50
11 52 46
12 49 46
13 40 37
14 38 33
15 51 39*

H=-13 K= 5
0 118 117
2 111 115
4 103 111
6 92 104
8 85 90
10 79 77
12 61 69
14 56 51
16 50 37*

H=-13 K= 6
1 54 48
3 53 50
5 48 50
7 36 39

H=-13 K= 7
2 31 32
9 41 42
11 48 44
13 51 45
15 46 39

H=-13 K= 9
0 98 103
2 99 106
4 93 91
6 92 81
8 68 78
10 79 78
12 57 61
14 55 53
16 49 38*

H=-13 K= 11
13 47 35*

H=-13 K= 13
0 72 81
2 51 74*
4 79 71
6 69 70
8 71 63
10 56 54
12 53 49

H=-13 K= 17
0 54 55
2 59 52
4 50 51
6 55 46
8 51 42

H=-12 K= 1
1 39 76*
2 18 15
3 62 99*
4 29 35
5 79 92
7 100 97
8 32 30
9 77 82
10 51 51
11 64 58
12 40 41
13 42 49
14 43 41
15 45 40
16 56 48
18 46 35*

H=-12 K= 3
1 76 105*
3 91 137*

H=-12 K= 4
2 27 32
4 36 34
6 47 46

H=-12 K= 5
1 71 75
3 41 48
5 48 55
6 32 33
7 57 52
8 50 52
9 48 46
10 55 58
11 41 41
12 46 50
14 50 47
16 54 47
18 52 44

H=-12 K= 7
1 112 131
3 133 124
5 107 113
7 114 120
9 104 105
11 86 80
13 71 64
15 49 49
17 52 40*

H=-12 K= 8
0 38 30*
2 35 37

H=-12 K= 9
12 47 44
14 60 50
16 53 45

H=-12 K= 11
1 104 100
3 101 99
5 113 103
7 98 96
9 89 84
11 75 64
13 47 49
15 49 43

H=-12 K= 15
1 81 75
3 65 70
5 72 71
7 68 66
9 53 56
11 50 52

H=-12 K= 19
5 52 45

H=-11 K= 0
4 59 49
10 48 50
12 53 53

H=-11 K= 1
0 37 80*
2 61 98*
4 79 97
6 84 90
8 66 93
9 38 33
10 52 58
12 53 49

H=-11 K= 2
1 83 157*
3 124 144
5 97 109
7 92 101
9 92 99
11 86 83
13 73 74
15 61 58

H=-11 K= 3
0 61 76
2 60 68
4 50 56
6 36 42
8 53 54
10 45 48

H=-11 K= 4
1 48 52
3 45 47
8 54 53
9 40 35
10 51 49

H=-11 K= 5
0 67 72
2 89 94
4 91 96
6 80 78
8 87 78
10 68 67
12 52 52
14 52 45

H=-11 K= 6
1 124 120
3 117 116
5 105 106
7 87 87
9 73 76
11 67 73
13 66 62

H=-11 K= 8
6 126 126
7 32 27
8 103 103
9 34 27
10 90 79
11 36 33
12 65 68
14 52 57
15 45 37
16 55 56
18 45 41

H=-10 K= 10
0 101 95
2 99 98
4 110 102
6 97 91
7 38 38
8 85 84
10 58 55
12 51 51
13 41 39
14 46 43
15 47 39
16 44 36
17 45 38

H=-10 K= 12
0 93 82
2 93 86
4 83 81
6 75 77
8 60 62
10 57 55
11 41 31*
12 46 45

H=-10 K= 14
0 97 93
2 82 88
4 95 83
6 72 78
8 65 68
10 56 61
12 53 50
14 50 42

H=-10 K= 18
0 45 67*
2 64 68
4 60 66
6 72 65
8 51 54
10 52 48

H=-10 K= 22
0 53 50
2 53 47
4 49 47
6 49 44

H=-9 K= 0
6 56 56
8 97 96
10 62 68
12 44 44
14 53 51
16 53 46
18 57 53
20 47 55
22 46 43

H=-9 K= 1
2 52 84*
4 64 73
5 33 40
6 94 97
7 26 35*
8 94 91
9 35 35
10 57 56
11 36 37
12 34 35
14 45 54
15 36 35
16 41 40

H=-9 K= 2
1 156 204*
3 188 194
5 149 159
7 100 133*
9 106 115
11 93 105
13 109 100
15 94 82
17 61 57
19 42 38
21 41 25*

H=-9 K= 3
0 70 79
2 70 80
4 67 78
5 33 46*
6 53 52
7 38 34
8 40 55*
9 43 43
10 54 53
11 37 33
12 46 42
13 37 38
15 37 34

H=-9 K= 4
1 33 41
2 33 37
3 59 61
4 47 49
5 65 66
6 41 44
7 51 48
8 38 35
9 26 31
10 71 63
12 66 60
13 32 25*
14 51 47
16 55 55
18 54 46
20 44 42
22 47 42

H=-9 K= 5
0 84 84
2 86 94
4 72 75
6 61 62
8 80 82
10 67 71
12 52 54
14 52 53
16 43 37

H=-9 K= 6
1 175 163
3 151 153
4 28 26
5 141 130
7 122 112
9 102 106
11 86 90
13 79 76
15 69 64
17 49 45

H=-9 K= 7
0 31 33
4 35 37
9 41 33*
11 41 40

H=-9 K= 8
1 93 90
3 90 89
5 65 62
7 62 59
8 54 49
9 66 60
11 42 45
12 40 42
13 49 44
14 47 44
15 44 41

H=-9 K= 9
0 111 90
2 107 92
4 112 106
6 98 83
8 67 71
10 65 61
12 53 55

H=-9 K= 10
1 122 123
3 91 88
5 69 72
7 71 68
9 72 63
11 67 69
13 62 58
15 42 40

H=-9 K= 12
1 100 98
3 85 79
5 73 74
7 58 65
9 60 60
11 63 62
13 55 50

H=-9 K= 13
0 84 79
2 74 74
4 69 67
6 60 64
8 62 52
10 41 48
12 43 41

H=-9 K= 14
1 46 47
3 60 53
5 47 47
7 45 35*

H=-9 K= 16
3 81 76
5 56 65
7 48 59
9 49 55

H=-9 K= 20
1 48 58
3 52 50

H=-8 K= 0
2 23 46*
4 48 62*
6 90 87
8 81 79
10 39 46
12 37 31
14 37 27*
16 44 39

H=-8 K= 1
1 78 154*
3 108 150*
5 90 108
6 25 27
7 151 137
8 35 41
9 116 123
10 47 44
11 66 83
12 52 52
13 70 67
14 62 65
15 55 51
16 48 54
17 46 42
18 48 45
20 47 46

H=-8 K= 2
0 30 44*
2 32 35
3 35 35
7 33 35

H=-8 K= 3
1 214 218
3 185 196
4 23 34*
5 172 176
7 180 162
9 150 157
10 44 44
11 112 113
12 45 44
13 72 79
14 41 40
15 72 62
16 41 42
17 46 44
19 42 39

H=-8 K= 4
0 58 65
2 77 88
4 100 93
6 83 79
8 55 51
10 38 40
12 42 43

H=-8 K= 5
1 36 47*
3 80 76
4 50 57
5 109 110
6 39 37
7 80 71
8 30 28
9 49 54
10 65 67
11 49 54
12 72 72
13 45 45
14 72 72
16 84 73
18 54 51
20 48 44

H=-8 K= 6
0 46 45
4 38 35
6 53 50

H=-8 K= 7
1 167 168
3 204 191
5 172 165
7 176 168
8 51 47
9 155 146
11 107 101
13 85 88
15 74 73
17 59 53
19 48 41

H=-8 K= 8
0 84 74
2 68 70
4 56 48
6 32 44*
8 37 42
10 52 52

H=-8 K= 9
6 44 43
8 60 66
10 59 62
12 48 59
14 51 58
16 55 53
18 58 54

H=-8 K= 10
4 38 32

H=-8 K= 11
1 129 126
3 120 127
5 147 145
7 111 122
9 91 100
11 109 100
13 88 80
15 61 57
17 54 48

H=-8 K= 12
4 42 34

H=-8 K= 13
10 48 46
12 50 49
14 53 45
16 50 44

H=-8 K= 14
2 45 39
4 42 37

H=-8 K= 15
1 94 92
3 87 98
5 96 95
7 99 89
9 72 78
11 75 63
13 50 50

H=-8 K= 19
1 60 64
3 55 54
5 60 56
7 56 53

H=-7 K= 1
0 118 229*
2 135 177*
4 119 140
5 28 27
6 140 133
7 59 66
8 170 168
9 50 42
10 120 149
11 61 63
12 124 121
13 70 59
14 84 82
15 57 54
16 64 64
17 40 40
18 45 45

H=-7 K= 2
1 34 36
2 37 41
3 80 82
4 24 29
6 69 74
7 74 72
8 31 33
9 55 52

H=-7 K= 3
0 104 104
2 124 123
3 49 48
4 130 133
5 54 47
6 143 131
7 65 60
8 96 98
9 94 90
10 77 81
11 89 92
12 63 64
13 75 85
14 66 62
15 82 75
16 46 46
17 53 53
18 39 32
19 47 52

Table 4. Continued.

H= -7 K= 4
1 39 37
3 48 47
4 42 38
5 30 25

H= -7 K= 5
0 206 194
2 229 208
4 206 210
6 206 200
8 190 183
9 48 46
10 144 143
12 185 175
14 101 96
16 80 75
17 45 31*
18 40 52*

H= -7 K= 6
1 81 73
3 77 78
4 26 35*
5 58 54
7 44 42
9 44 49

H= -7 K= 7
0 62 61
2 75 81
4 87 78
5 40 40
6 63 65
7 60 62
8 34 37
9 73 69
10 36 40
11 86 77
13 82 77
15 62 67
17 67 63
19 55 50
21 57 49

H= -7 K= 8
3 58 45*
5 33 31

H= -7 K= 9
0 201 191
2 127 190*
4 218 174*
6 135 165
8 124 136
10 113 130
12 109 106
14 82 86
16 67 57
18 46 44

H= -7 K= 10
1 32 41*

H= -7 K= 11
9 59 62
11 62 57
13 42 51
15 44 45
17 51 49
19 49 48

H= -7 K= 13
0 125 128
2 137 134
4 149 137
6 124 120
8 111 104
10 100 90
12 81 81
14 65 62
16 52 47

H= -7 K= 15
11 50 45
13 52 43

H= -7 K= 17
0 102 95
2 86 84
4 83 76
6 71 71
8 67 71
10 53 64
12 54 54

H= -6 K= 0
4 176 216
6 130 135
8 151 142
10 144 149
12 144 138
14 98 108
16 76 80
18 49 52
20 48 43

H= -6 K= 1
5 119 127
6 45 46

7 155 163
9 106 109
11 53 54
12 49 49
13 40 37
14 64 55
16 45 46

H= -6 K= 2
3 38 45
4 40 55*
5 53 55
7 73 67
9 85 87
11 86 82
12 38 34
13 52 55
15 73 65
17 67 62
19 66 58
21 55 50

H= -6 K= 3
1 151 151
2 32 34
3 113 113
5 169 172
7 123 135
8 48 54
9 81 94
10 35 35
11 84 75
13 48 54
15 57 53

H= -6 K= 4
0 196 175
2 238 235
3 38 42
4 239 220
6 182 177
7 26 24
8 179 159
9 34 36
10 122 116
12 101 101
14 102 96
16 66 71
18 50 53

H= -6 K= 5
3 59 66
4 36 39
5 75 78
6 24 24
8 44 48
9 32 39
11 54 61
12 40 40
14 48 44

H= -6 K= 6
0 68 67
2 76 79
3 49 47
4 100 96
5 74 69
6 64 64
7 37 41
8 64 62
9 37 48*
10 49 50
11 47 52
13 66 67
14 45 44
15 66 58
17 50 54
19 49 46

H= -6 K= 7
1 119 120
3 115 121
5 135 127
7 125 130
9 109 102
10 47 35*
11 97 88
13 65 63

H= -6 K= 8
0 237 214
2 171 167
4 115 118
6 120 125
8 114 105
10 97 107
12 73 79
14 56 63
16 46 47

H= -6 K= 9
4 48 47
10 51 49
12 45 46
14 53 49
16 56 53

H= -6 K= 10
0 128 116
2 130 119

8 81 77
6 74 70
7 45 45
8 65 72
9 36 37
10 68 71
12 51 60
13 44 39
14 50 50

H= -6 K= 11
1 87 84
3 107 118
5 120 119
7 102 97
9 90 91
11 79 71
13 50 54
15 48 44

H= -6 K= 12
0 84 88
2 84 85
4 94 86
6 89 72
8 55 57
12 51 50

H= -6 K= 13
10 46 38

H= -6 K= 14
0 106 99
2 101 93
4 87 92
6 89 87
8 84 73
10 62 60
12 45 48

H= -6 K= 15
1 81 74
3 64 63
5 50 61
7 67 68
9 53 59
11 50 47

H= -6 K= 18
0 88 78
2 66 72
4 72 69
6 67 60
8 53 53
10 54 47

H= -6 K= 19
3 52 43
5 49 41

H= -6 K= 22
0 52 48
2 52 47

H= -5 K= 0
4 151 157
6 82 79
8 83 83
10 94 94
12 86 86
14 103 103
16 112 105
18 87 91
20 66 72
22 59 65
24 53 54

H= -5 K= 2
4 21 15*
5 310 302
6 33 32
7 257 236
9 193 199
11 180 173
13 92 159*
15 111 107
17 84 84
19 59 62
21 49 42

H= -5 K= 3
2 26 25
4 23 21
6 24 27

H= -5 K= 4
1 82 75
2 76 83
3 92 96
4 32 29
5 74 76
6 78 77
7 29 31
8 74 83
9 30 37
10 82 79
11 47 51
12 98 86
14 76 71
16 83 72

18 75 78
20 67 72
22 51 55

H= -5 K= 5
0 65 50*
4 32 34

H= -5 K= 6
1 282 263
3 244 209
5 201 192
7 199 171
8 44 40
9 152 151
11 139 139
13 120 120
15 112 97
17 93 75
19 52 55

H= -5 K= 7
0 48 45
4 53 45

H= -5 K= 8
1 198 186
3 139 132
4 67 70
5 121 118
6 70 68
7 131 116
8 48 53
9 98 94
10 47 51
11 71 80
12 55 56
13 71 62
14 59 68
15 47 42
16 63 60
17 42 38
18 48 49

H= -5 K= 9
0 34 28

H= -5 K= 10
1 130 152
2 34 33
3 161 154
4 49 45
5 156 132
6 46 49
7 133 131
8 37 34
9 117 114
10 51 49
11 68 81
12 54 58
13 75 73
14 48 50
15 64 70
16 47 49
17 44 53

H= -5 K= 12
1 114 137
3 138 134
5 142 121
6 43 42
7 123 107
8 53 48
9 99 99
10 47 42
11 62 78*
12 45 38
13 65 67
14 47 37*
15 57 62

H= -5 K= 14
1 86 85
3 83 81
5 85 81
6 43 38
7 62 62
8 53 47
9 42 48
9 45 48
11 61 51
13 49 43
14 50 43

H= -5 K= 16
1 98 100
3 99 100
5 101 95
7 73 89
9 69 75
11 60 69
13 57 60
15 54 48

H= -5 K= 20
1 80 77
3 85 81
5 63 75
7 53 65
9 54 58

H= -5 K= 24
1 56 53
3 47 48

H= -4 K= 0
4 297 254
6 282 287
8 215 168*
10 172 161
12 124 116
14 125 124
16 106 109
18 71 74
20 57 46

H= -4 K= 1
4 54 50
5 110 92
7 98 95
8 50 49
9 102 95
10 112 100
11 91 83
12 68 65
13 85 76
14 45 43
15 55 48
16 49 45

H= -4 K= 2
3 70 64
4 80 85
5 88 89
6 80 73
7 103 107
9 83 83
11 85 74
13 93 84
15 61 67
16 49 46*
17 72 75
19 65 68
21 54 54

H= -4 K= 3
2 41 41
3 189 147*
4 38 36
5 185 154
6 32 34
7 97 104
8 73 70
9 106 109
10 56 50
11 87 95
12 32 44*
13 70 77
15 56 59

H= -4 K= 4
0 305 279
1 42 41
2 311 285
3 24 28
4 286 247
5 35 36
6 225 199
7 39 37
8 138 152
9 43 42
10 141 140
12 170 156
14 93 96
16 60 70
18 59 64
20 49 43
22 44 31*

H= -4 K= 5
1 94 99
3 58 48
5 88 83
6 27 25
7 69 68
8 49 50
9 51 47
10 43 53
12 43 41
14 40 39
18 50 37*

H= -4 K= 6
0 159 165
2 60 70
3 58 59
4 65 62
5 56 42*
6 98 99
7 72 69
8 49 47
9 55 62
10 89 77
11 51 57
12 71 66
13 55 56
15 68 67
17 54 61
19 68 60

H= -4 K= 7
1 159 147
3 137 136
5 107 111
7 117 120
9 109 101
11 88 83
13 70 77
15 47 57

H= -4 K= 8
0 260 219
2 242 188*
4 193 177
6 131 141
7 67 62
8 138 141
10 107 107
12 67 68
13 38 33
14 60 68
16 65 69
18 49 42

H= -4 K= 9
8 31 43*
10 54 57
12 49 54
14 44 46
16 43 39

H= -4 K= 10
0 96 101
2 119 117
4 130 132
5 51 49
6 106 101
8 87 87
10 52 64
12 60 65
13 37 39
14 41 48
15 42 49
16 48 47

H= -4 K= 11
1 172 145
3 128 124
5 113 106
7 89 92
9 89 87
11 55 70*
13 49 57
15 44 49

H= -4 K= 12
0 99 104
2 111 113
4 86 81
6 81 72
8 74 74
10 56 61
12 59 53
14 44 47
15 41 42

H= -4 K= 13
12 40 40

H= -4 K= 14
0 141 135
2 123 115
4 86 93
6 105 90
8 88 86
10 73 75
12 49 56

H= -4 K= 15
1 81 82
3 63 66
5 50 65*
7 55 62
9 48 54
11 50 55

H= -4 K= 16
2 46 39

H= -4 K= 18
0 84 77
2 84 85
4 71 77
6 67 72
8 48 64*
10 45 54

H= -4 K= 22
0 56 51
2 51 52
4 52 51
6 48 44

H= -3 K= 0
4 85 83
6 37 39
8 47 47

H= -3 K= 1
5 53 49

6 328 267
7 58 50
8 227 196
10 181 172
11 55 48
12 107 107
13 72 69
14 111 84*
15 75 70
16 69 66
17 63 65
18 55 58
19 44 44

H= -3 K= 2
3 139 125
4 42 40
5 136 128
6 25 23
7 47 50
9 31 32
11 75 78
13 58 54

H= -3 K= 3
1 43 53
2 133 116
3 92 83
4 133 127
6 190 166
8 167 153
9 105 106
10 118 115
11 97 100
12 104 92
13 102 101
14 52 53
15 70 78
16 47 45
17 83 78
18 47 40
19 58 64
21 48 52
23 47 45

H= -3 K= 4
1 83 73
2 51 46
3 110 86*
5 103 109
6 30 35
8 30 25
11 36 41
12 37 40

H= -3 K= 5
1 58 55
2 365 307
4 274 254
6 274 241
7 51 48
8 215 201
9 51 64
10 189 191
11 43 48
12 181 165
13 33 40
14 118 95
16 58 63
18 57 58
20 47 43

H= -3 K= 6
1 118 119
3 93 89
5 83 87
7 85 87
9 58 64
11 41 40
13 37 43
15 41 47

H= -3 K= 7
0 27 29
2 62 68
4 94 95
5 44 48
6 54 70*
7 94 104
8 75 76
9 63 61
10 34 31
11 92 84
13 91 92
14 43 43
15 73 88
17 69 74
19 67 67
21 50 52

H= -3 K= 8
1 55 54
2 25 29
3 27 31
4 33 32
5 43 43
6 44 60*
7 35 34
8 39 49

H= -3 K= 9
0 190 179
2 176 178
4 246 223
6 265 228
8 225 210
10 135 141
12 102 98
14 80 90
16 75 86
18 52 58

H= -3 K= 10
1 66 65
3 53 61
5 36 36
7 41 42
9 55 55
11 63 65
13 61 67
15 65 73
17 69 62
19 47 50

H= -3 K= 11
5 47 51
7 41 42
9 55 55
11 63 65
13 61 67
15 65 73
17 69 62
19 47 50

H= -3 K= 12
1 44 49
7 43 39

H= -3 K= 13
0 129 141
2 155 151
4 172 147
6 149 143
8 129 130
10 123 113
12 83 93
14 57 71*
16 46 53
18 48 46

H= -3 K= 15
0 46 52
6 37 36
7 45 40
8 42 35
9 42 48
13 45 49
15 47 46

H= -3 K= 16
1 40 42
3 49 46

H= -3 K= 17
0 85 92
2 93 99
4 107 98
6 95 94
8 82 83
10 71 72
12 52 53
14 49 45

H= -3 K= 19
2 42 47
4 50 48
6 51 47

H= -3 K= 21
0 48 49
2 49 50
4 53 52
6 49 48

H= -3 K= 23
2 46 43

H= -2 K= 0
4 144 127
6 108 99
8 65 66
10 31 30
14 58 55
16 49 54

H= -2 K= 1
5 121 122
6 79 73
7 222 201
8 130 108
9 164 159
10 93 81
11 138 131
12 105 105
13 121 111
14 90 84
15 79 76
16 49 56
17 56 64
18 54 65
20 49 57

H= -2 K= 2
3 128 108
4 105 106

Table 4. Continued.

6 104 96	9 253 201*	13 53 68*	14 48 46	17 49 46	6 103 93	3 36 41	17 44 50
8 61 55	10 36 33	15 46 58*	15 39 38	21 47 34*	8 85 94	4 423 386	18 45 43
12 38 41	11 188 165		16 44 37		10 68 71	6 306 285	19 51 50
	13 124 122	H= -2 K= 17	17 50 45	H= -1 K= 8	12 46 55	8 223 216	
H= -2 K= 3	15 74 66	1 45 52	19 54 51	1 104 106	14 48 48	9 71 72	H= 0 K= 12
1 188 200*	17 86 73	3 45 51		3 101 92		10 171 165	0 134 125
2 27 23	19 55 50	5 46 47	H= -1 K= 4	4 56 58	H= -1 K= 14	12 189 163	2 144 152
3 293 226*			1 136 119	5 147 114*	1 66 64	13 36 43	4 127 137
7 274 245	H= -2 K= 8	H= -2 K= 19	2 116 105	6 29 34	3 73 71	14 137 142	6 94 92
8 44 42	0 79 66	1 75 76	3 26 30	7 111 120	5 65 61	16 115 110	7 56 60
9 185 177	2 68 65	3 75 74	4 70 58	8 47 44	7 48 53	18 78 79	8 105 100
10 76 66	4 85 81	5 59 69	5 44 49	9 82 84	9 45 52	20 52 50	9 90 80
11 199 188	6 33 40	7 54 61	6 101 100	10 46 46	11 47 40		10 60 73
12 71 59	8 46 46	9 56 57	7 49 52	11 52 60	13 41 33*	H= 0 K= 6	11 51 53
13 117 130	10 53 49	11 57 52	8 67 75	12 35 42		0 330 311	12 92 73*
14 50 53			9 52 54	13 47 48	H= -1 K= 16	1 48 51	13 42 47
15 101 94	H= -2 K= 9	H= -2 K= 21	10 88 78	14 49 56	1 106 103	2 134 141	14 72 74
16 46 47	3 47 52	1 51 47	11 55 62	16 53 58	3 122 107	3 84 82	15 48 41
17 68 68	6 42 36	3 56 47	12 98 89	17 46 43	5 92 91	4 90 89	16 45 51
19 47 48	7 51 51		13 36 42	18 47 58	7 83 82	5 78 73	17 46 51
	8 74 79	H= -1 K= 0	14 64 70	20 46 49	9 75 74	6 122 116	19 45 50
H= -2 K= 4	9 35 41	4 222 189	16 75 76		11 55 59	7 59 61	
0 217 191	10 74 84	6 211 179	18 62 73	H= -1 K= 9	13 48 48	8 93 101	H= 0 K= 14
1 49 47	12 87 83	8 159 121*	20 52 60	0 226 200		9 97 106	0 125 149
2 187 142*	14 81 81	12 72 65	22 46 48	2 158 154	H= -1 K= 17	10 83 90	2 122 126
3 58 59	16 67 66	14 111 112	24 45 39	4 100 101	0 60 57	11 76 74	4 128 135
4 83 83	18 55 58	16 86 88		6 141 136	2 51 57	12 33 42*	6 135 120
5 35 42	20 49 55	18 79 75	H= -1 K= 5	8 108 127	4 52 60	13 53 59	8 106 103
6 78 70	22 47 51	20 66 60	0 64 73	10 118 122	6 48 52	14 47 42	10 74 88
8 64 68			2 88 121*	12 76 85	8 54 53	15 75 67	11 47 42
10 60 62	H= -2 K= 10	H= -1 K= 1	3 61 60	14 50 55	10 47 44	16 60 56	12 57 74*
12 76 70	2 32 35	4 318 234*	4 231 196		12 44 37	17 81 84	13 53 51*
	4 43 44	5 33 33	5 47 48	H= -1 K= 10		19 67 67	14 77 72
H= -2 K= 5		6 253 221	6 188 185	1 153 142	H= -1 K= 20	21 60 58	16 47 59
1 101 102	H= -2 K= 11	7 123 115	7 39 47	2 33 40	1 68 66	23 53 49	17 48 25*
2 79 73	1 225 201	8 125 110	8 136 124	3 176 164	3 57 65	25 51 41	18 49 41
3 165 153	2 40 36	9 36 42	10 91 90	5 166 140	5 63 64		
4 33 32	3 143 190*	10 100 98	11 37 36	6 32 33	7 54 60	H= 0 K= 8	H= 0 K= 16
5 186 162	5 147 156	11 44 51	12 88 76	7 113 122	9 50 53	0 250 222	0 89 78
6 72 67	7 158 154	12 121 111	13 34 46*	9 107 98		2 235 211	2 63 60
7 89 83	9 147 144	13 49 54	14 71 71	11 62 72	H= 0 K= 0	4 212 204	4 42 43
8 102 88	11 138 129	14 40 43	16 59 66	13 60 59	4 239 222	6 194 175	6 43 38
9 98 97	13 109 103	15 58 54	18 41 42	14 40 33	6 271 274	7 60 58	8 44 46
10 84 99	15 78 78	17 45 49		15 41 45	8 316 258	8 115 121	10 45 39
11 71 83	17 43 54*	18 39 38	H= -1 K= 6	17 44 39	10 267 269	9 56 53	11 42 48
12 116 117	19 46 42		1 366 286*	18 45 42	12 239 212	10 151 149	13 44 39
13 42 51		H= -1 K= 2	3 265 270		14 124 129	11 57 56	
14 96 96	H= -2 K= 12	3 196 247*	4 68 60	H= -1 K= 11	16 124 111	12 136 133	H= 0 K= 18
15 42 40	0 42 47	4 55 49	5 305 235*	7 32 33	18 124 111	13 61 57	0 131 116
16 73 82	2 39 37	5 336 271	6 82 75	9 51 50	18 66 67	14 107 112	2 116 109
18 72 75	3 36 35	6 46 47	7 180 168	11 45 48	20 51 43	15 36 44	4 83 93
20 55 59		7 278 254	8 56 57	13 57 58		16 68 80	6 60 76*
22 49 51	H= -2 K= 13	8 53 49	9 117 133	15 39 48	H= 0 K= 2	17 46 45	8 79 81
24 51 46	1 41 37	9 207 195	11 123 122	17 41 39	3 58 48	18 56 65	10 57 71
	3 41 42	10 36 37	13 116 106		4 63 46*	20 42 42	12 59 65
H= -2 K= 6	10 65 62	11 164 156	14 47 51	H= -1 K= 12	5 89 84		14 55 54
0 100 126*	12 57 61	13 124 117	15 82 84	1 124 128	7 140 147	H= 0 K= 10	
1 29 30	14 46 55	15 118 103	17 52 59	2 37 34	8 56 55	0 156 168	H= 0 K= 22
2 73 74	16 53 54	17 83 95	19 47 45	3 126 130	9 74 68	2 205 189	0 89 76
3 75 69	18 51 46	19 58 65		4 38 36	11 116 104	4 159 166	2 88 74
4 30 25			H= -1 K= 7	5 134 126	12 51 54	5 59 42*	4 66 67
5 28 26	H= -2 K= 14	H= -1 K= 3	0 83 76	7 103 93	13 139 132	6 144 138	6 51 60
6 35 42	0 51 47	2 172 147	2 55 55	9 70 74	15 99 98	7 66 80	8 47 54
7 40 42	2 39 40	4 152 146	4 37 28*	11 70 72	17 95 79	8 80 86	10 48 48
9 31 40*		5 90 74	5 41 44	13 59 60	19 90 89	9 90 93	12 48 41
11 40 47	H= -2 K= 15	6 167 147	7 34 36	15 44 44	21 63 81*	10 92 101	
	1 121 126	7 66 64	8 35 31	16 45 40	23 61 71	11 67 70	H= 0 K= 26
H= -2 K= 7	3 151 134	8 130 129	10 49 50		25 46 53	12 107 112	0 48 41
1 316 284	5 120 118	9 75 81	11 46 50	H= -1 K= 13		13 50 48	2 48 41
3 297 265	7 142 120	10 76 90	12 37 40	0 89 86	H= 0 K= 4	14 73 74	
5 263 221	9 98 106	11 46 46	13 65 68	2 121 107	0 293 268	15 41 47	
7 246 231	11 60 75	13 46 37*	15 54 52	4 134 114	2 367 406	16 43 46	

weights chosen according to Cruickshank.[9] In addition, the reflexions not obeying the condition $0.80 \leq |F_o|/|F_c| \leq 1.25$ were given zero weight. The atomic scattering factors for the neutral atoms were taken from International Tables [10] for oxygen and carbon and from Cromer *et al.*[11] for neodymium.

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 0.098 and 0.097, respectively. All observed reflexions were included in the calculation of R. Further refinement using anisotropic thermal parameters for neodymium and an over-all scale factor resulted in $R = 0.092$ and $wR = 0.091$. The shifts of all parameters were less than 5 % of their estimated standard deviations in the last cycle of refinement.

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 $\sin\theta$ intervals (Table 2).

The final atomic parameters with their estimated standard deviations are given in Table 3. The electron density maps of a difference synthesis based upon these parameters showed a peak of about 4.5 e/Å^3 at the position of neodymium, and only spurious peaks less than 2 e/Å^3 in the other regions. 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 DRF, LALS, DISTAN, PLANE, CELSIUS, and ORTEP.[12]

DESCRIPTION OF THE STRUCTURE

The general features of the structure of NDO are shown in Figs. 1 and 2. Interatomic distances and angles are given in Table 5; some of them are also indicated in Figs. 4 and 5. The numbering of the atoms constituting the two

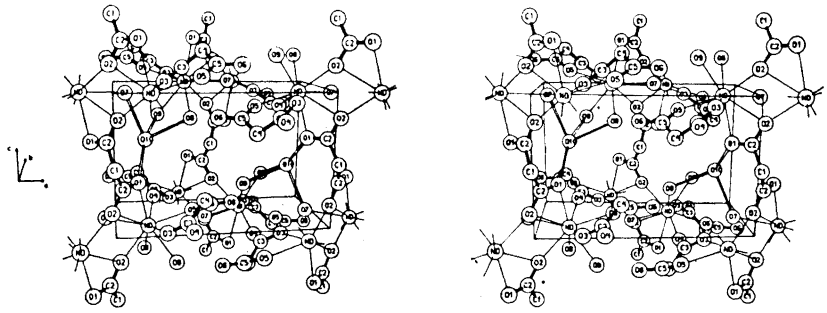

Fig. 1. A stereoscopic pair of drawings showing part of two adjacent neodymium-malonate networks and the bonding between them. Bonds within the malonate ions are filled, hydrogen bonds are open, and Nd – O bonds are single lines. The intra-network hydrogen bonds are omitted for clarity. The box outlined is $0 \leq x \leq 1$, $0 \leq y \leq 1/2$, $0 \leq z \leq 1/2$.

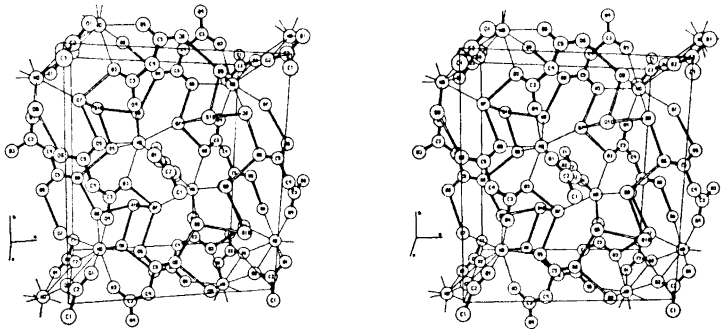

Fig. 2. A stereoscopic pair of drawings illustrating the neodymium-malonate network around $z = 0$. The bonds are indicated in the same way as in Fig. 1. The box outlined is $0 \leq x \leq 1$, $0 \leq y \leq 1$, $-1/4 \leq z \leq 1/4$.

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

A. The coordination polyhedron

Nd – O(1)	2.54(1)	$O(2^{i}) - O(7)$	3.03(2)
$Nd - O(2^{i})$	2.46(1)	$O(2^{i}) - O(8)$	3.24(2)
Nd – O(3)	2.47(1)	$O(2^{i}) - O(9)$	3.07(2)
$Nd - O(4^{vi})$	2.41(1)	$O(2^{i}) - O(2)$	2.71(2)
Nd – O(5)	2.43(1)	O(3) – O(5)	2.83(2)
Nd – O(7)	2.53(1)	O(3) – O(9)	2.92(2)
Nd – O(8)	2.46(1)	O(3) – O(2)	2.91(2)
Nd – O(9)	2.49(1)	$O(4^{vi}) - O(5)$	2.86(2)
Nd – O(2)	2.72(1)	$O(4^{vi}) - O(7)$	2.97(2)
O(1) – O(3)	3.16(2)	$O(4^{vi}) - O(8)$	2.97(2)
$O(1) - O(4^{vi})$	3.05(2)	O(5) – O(8)	3.93(2)
O(1) – O(5)	3.31(2)	O(5) – O(9)	2.92(2)
O(1) – O(7)	3.24(2)	O(7) – O(8)	2.97(2)
O(1) – O(2)	2.18(2)	O(7) – O(2)	2.90(2)
$O(2^{i}) - O(3)$	3.07(2)	O(8) – O(9)	2.71(2)

B. Ligand 1

C(1) – C(2)	1.51(2)	$\angle C(2) - C(1) - C(2^{ii})$	113(2)
C(2) – O(1)	1.22(2)	$\angle O(1) - C(2) - O(2)$	122(1)
C(2) – O(2)	1.28(2)	$\angle C(1) - C(2) - O(1)$	120(1)
		$\angle C(1) - C(2) - O(2)$	119(1)

C. Ligand 2

C(4) – C(3)	1.53(2)	$\angle C(3) - C(4) - C(5)$	117(1)
C(4) – C(5)	1.52(3)	$\angle O(3) - C(3) - O(4)$	121(1)
C(3) – O(3)	1.29(2)	$\angle C(4) - C(3) - O(3)$	119(1)
C(3) – O(4)	1.26(2)	$\angle C(4) - C(3) - O(4)$	120(1)
C(5) – O(5)	1.26(2)	$\angle O(5) - C(5) - O(6)$	123(2)
C(5) – O(6)	1.20(3)	$\angle C(4) - C(5) - O(5)$	118(2)
		$\angle C(4) - C(5) - O(6)$	119(2)

D. Possible hydrogen bonds

$O(7) - O(3^{i})$	2.63(2)	O(8) – O(10)	2.71(2)
$O(7) - O(5^{v})$	2.77(2)	$O(9) - O(6^{iii})$	2.76(2)
$O(7) - O(10^{v})$	2.85(2)	O(9) – O(10)	2.76(2)
$O(8) - O(6^{v})$	2.67(2)	$O(10) - O(1^{viii})$	2.79(2)

structurally independent malonate ions, referred to as ligand 1 and ligand 2, is shown in Fig. 4. The superscripts $(i) - (x)$ refer to the following equivalent sites in the structure:

	x,y,z	(iv)	$1/2+x,1/2-y,\bar{z}$	$(viii)$	$1/2-x,1/2-y,z-1/2$
(i)	$\bar{x},\bar{y},\bar{z}$	(v)	$x-1/2,1/2-y,\bar{z}$	(ix)	$x,\bar{y},1/2+z$
(ii)	$\bar{x},y,1/2-z$	(vi)	$1/2-x,1/2+y,z$	(x)	$1/2-x,y-1/2,z$
(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 neodymium ions are situated at $z \approx 0$ and $z \approx 1/2$. Those at the same z-level are coupled in pairs by oxygen bridges Nd – O(2) – Nd, where O(2) is a carboxylate oxygen of ligand 1, as shown in Fig. 1. The methylene carbon of this ligand is situated on the twofold axis $x = 0$, $z = 1/4$, and hence ligand 1 connects the neodymium pairs in the z-direction. Ligand 2 links the neodymium pairs in layers parallel to (001) by bridges of the type Nd – OCO – Nd. As illustrated in Fig. 2, each neodymium pair is bonded in this way to four adjacent pairs.

There is a system of hydrogen bonds within the layer, formed by the coordinated water molecules O(7), O(8), and O(9) with the carboxylate oxygens of ligand 2 as acceptors. The uncoordinated water molecule O(10) is situated between the layers at $z \approx 1/4$ (see Fig. 1). It is hydrogen bonded to the coordinated water molecules in one layer and to the carboxylate oxygen O(1) in an adjacent layer. The layers are thus held together by ligand 1 as described above and by hydrogen bonds *via* O(10).

The coordination polyhedron. The coordination around the pair of neodymium ions is shown in Fig. 3, and the dimensions of the coordination polyhedron are given in Table 5 A. Each neodymium ion is coordinated by six carboxylate oxygens, from four malonate ions, and by three water oxygens. These nine oxygens form a distorted monocapped square antiprism.

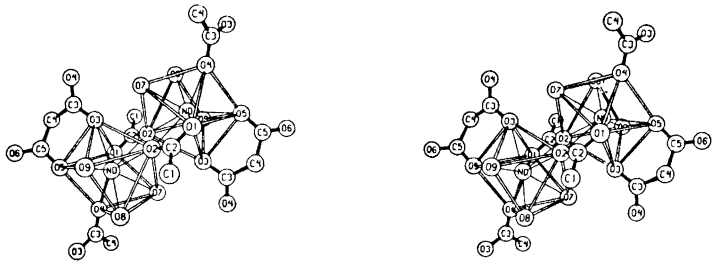

Fig. 3. A stereoscopic pair of drawings showing the coordination polyhedra around the neodymium ions Nd and Nd^{i}. Nd – O bonds are single lines, the bonds within the malonate ions are filled and the edges of the square antiprism are open.

The carboxylate oxygens O(2) and O(2^{i}) form asymmetric oxygen bridges between the two neodymium ions; the distances Nd – O(2) and Nd – O(2^{i}) are 2.72 Å and 2.46 Å, respectively. The other Nd – O bond distances are in the range 2.41 – 2.54 Å and the average of the nine Nd – O distances, 2.50 Å, is compatible with those found in other structures containing neodymium coordinated by nine oxygens.[13]

The "square" faces of the coordination polyhedron are O(8) – O(4^{vi}) – O(5) – O(9) and O(7) – O(1) – O(3) – O(2^{i}). The distant oxygen O(2) caps the latter square, which is larger than the first one, the edge lengths being in the intervals 2.71 – 2.97 Å and 3.02 – 3.24 Å, respectively. The "square" faces are approximately planar (see Table 6) and the least-squares planes through the atoms forming the "squares" are parallel. The neodymium ion is 0.2 Å closer to the capped square than to the uncapped one. The mean "contact"

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)	−0.03
C(2)	0.00	C(3)	0.01	C(5)	−0.03	C(5)	0.03
O(1)	−0.00	O(3)	−0.01	O(5)	0.01	O(3)	0.03
O(2)	−0.00	O(4)	−0.01	O(6)	0.01	O(5)	−0.03
*		*		*		*	
Nd	0.67	Nd	−0.03	Nd	0.49	Nd	−0.42
Nd	0.03	Nd^{x}	0.82			C(4)	−0.50

B. The coordination polyhedron

Atom	Distance	Atom	Distance
O(3)	0.22	O(8)	0.08
O(1)	−0.20	$O(4^{vi})$	−0.08
O(7)	0.21	O(5)	0.08
$O(2^{i})$	−0.23	O(9)	−0.08
*		*	
Nd	1.19	Nd	−1.38

distance between oxygens not belonging to the same malonate ion is 3.00 Å as compared to 2.98 Å in $Nd_2(C_2O_4)_3.10.5H_2O$.[2] Only two of the O − O distances are shorter than 2.8 Å, *viz.* O(2) − $O(2^{i})$ and O(8) − O(9), both being 2.71 Å.

Ligand 2 forms a six-membered chelate ring with neodymium. Its bite is 2.83 Å. The ring has a boat conformation with the four atoms O(3), C(3), C(5), and O(5) coplanar within ± 0.03 Å and the atoms Nd and C(4) situated 0.42 and 0.50 Å at the same side of this plane (Table 6). A similar conformation is found for the two structurally independent malonate rings of the complex $Comal_2en^{-}$ (en = $H_2NCH_2CH_2NH_2$), while the three equivalent rings of $Crmal_3^{3-}$ have the methylene carbon 0.69 Å out of the plane formed by the other five atoms.[5]

The polyhedra around Nd and Nd^{i} share the edge O(2)···$O(2^{i})$ and the distance Nd···Nd^{i} is relatively short, 4.42 Å. The carboxylate group C(2)O(1)O(2) may be described as bridging-chelating, *i.e.* both oxygens are bonded to the same metal ion in a four-membered ring and one of them, O(2), forms an additional bond to the second metal ion. This type of bridge is not uncommon in lanthanoid carboxylate structures. It is found, *e.g.*, in $Nd(OCOCH_2NHCH_2OCO)Cl.3H_2O$,[14] $K_2Ce(CH_3COO)_5.H_2O$,[15] and $Ce(CH_3COO)_3.0.7H_2O$.[16] The next shortest Nd···Nd distance, 6.70 Å, is between the neodymium ions Nd and Nd^{vi} which are connected by the bridging carboxylate group O(3)C(3)O(4) (see Fig. 2).

The malonate ions. The dimensions of the malonate ions are given in Table 5 B,C and in Fig. 4. The corresponding bond distances and angles in the two ions are equal within the limits of errors. There are no previous reports giving the

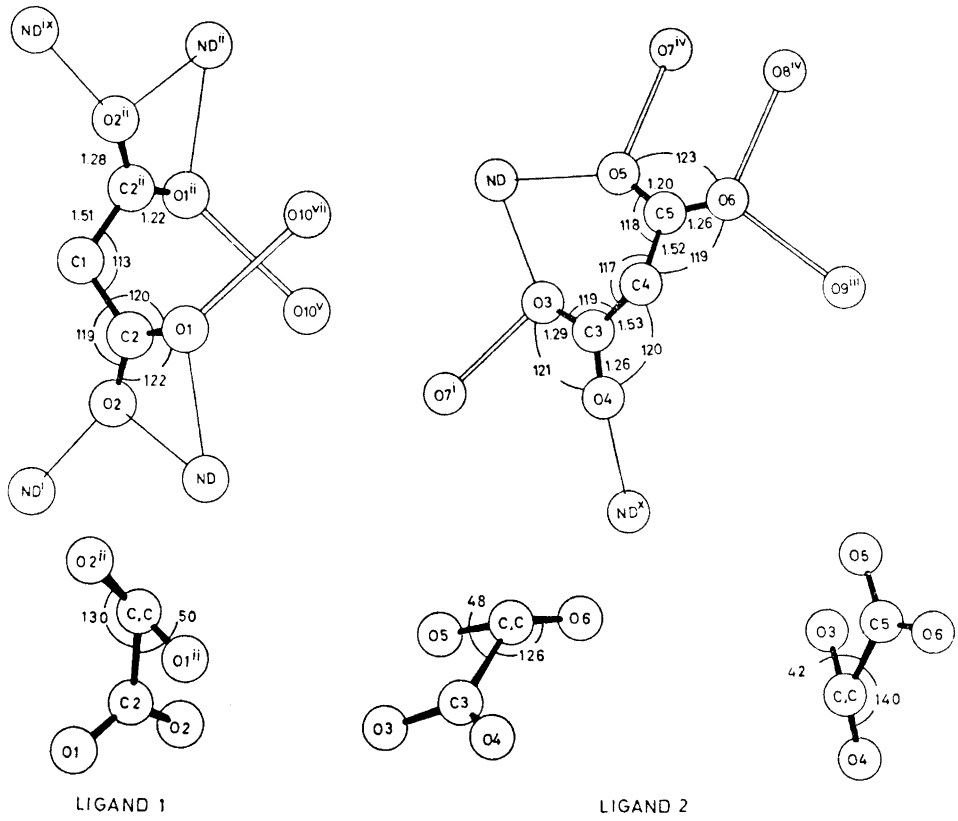

Fig. 4. The two malonate ions and their immediate surroundings, together with projections of each malonate ion along its C–C bonds. The angles indicated in the projections are the dihedral angles C–C–C–O.

dimensions of malonate ions. (The report of $Comal_2en^-$ and $Crmal_3^{3-}$ referred to above is only preliminary and contains no distances or atomic coordinates.) A comparison with the malonate residue in the compound $KOOCCH_2COOH$ [17] shows significant differences in the C – C – O bond angles attributable to the non-equivalence of the two C – O bonds in the hydrogen malonate ion, but otherwise the dimensions of the ions are compatible.

The three independent C–COO groups are planar within the limits of errors (Table 6) while the malonate ions are both nonplanar. In ligand 1 the dihedral angle $C(2^{ii}) - C(1) - C(2) - O(2)$ is 130°. Since the methylene carbon is situated on a two-fold axis, this means that the two COO-groups are twisted 50° in opposite directions out of the plane of the three central carbon atoms. Thus the two C–COO-planes are almost perpendicular to each other and the oxygens of the two COO-groups are well separated; the shortest distances are $O(1)\cdots O(1^{ii})$: 3.24 Å and $O(1)\cdots O(2^{ii})$: 3.78 Å.

In ligand 2, which forms the six-membered chelate ring, the dihedral angles O(3)–C(3)–C(4)–C(5) and C(3)–C(4)–C(5)–O(5) are 42° and 48°, respectively, *i.e.* the two COO-groups are twisted in the same direction out of the plane of the carbon atoms by about 45°. This twist results in one short O–O distance, *viz.* the ligand bite O(3)···O(5) which is 2.83 Å.

The conformations of the malonate ions may be compared with those found for the malonate residues in malonic acid [18] and potassium hydrogen malonate.[17] In malonic acid one COO-group but not the other is twisted about 90° out of the plane of the carbon atoms while the atoms of the malonate group in potassium hydrogen malonate are almost coplanar. In the latter compound, the shortest intramolecular separation of oxygens belonging to different COO-groups is 2.80 Å.

The hydrogen bonds. The possible hydrogen bond distances, *i.e.* the $(H_2)O-O$ distances shorter than 3.20 Å, between oxygens not belonging to the same coordination polyhedron [19] are given in Table 5 D. There is just one suitable distance for each of the active hydrogen atoms, and the longest of these distances is 2.85 Å. Thus the choice of a probable hydrogen bond system seems to be unequivocal even though the positions of the hydrogen atoms have not been located. The hydrogen bond system is illustrated in Fig. 5.

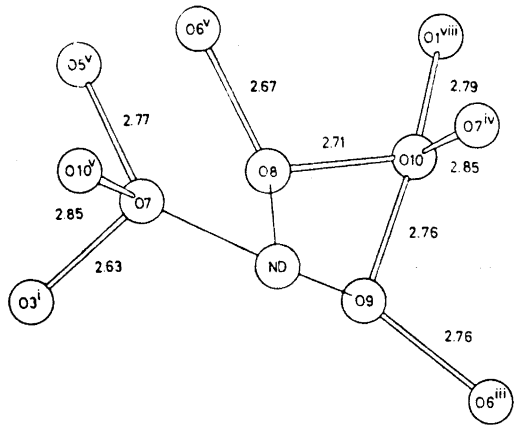

Fig. 5. The immediate surroundings of the four water molecules. Hydrogen bonds are open and Nd–O bonds are single lines.

The water molecule O(7) forms two hydrogen bonds to carboxylic oxygens within the neodymium malonate layer, *viz.* O(7)···O(3^i) and O(7)···O(5^v), and accepts one hydrogen bond from the uncoordinated water molecule O(10). The donor angle O(5^v)–O(7)–O(3^i) is 98°. The three hydrogen bonds and the bond Nd–O(7) are approximately tetrahedrally arranged around O(7) and the "tetrahedral" angles are in the range 95–133°. The oxygens O(7) and O(3^i) belong to different coordination polyhedra of an edge-sharing pair and thus the bond O(7)···O(3^i) constitutes an additional link between these polyhedra.

The water molecules O(8) and O(9) each form one intra-layer hydrogen bond to a carboxylic oxygen, *viz.* O(8)···O(6^{ii}) and O(9)···O(6^{iii}), and one to the water molecule O(10). The donor angles O(6^{ii}) – O(8) – O(10) and O(6^{iii}) – O(9) – O(10) are 111° and 112° respectively and the sum of the three bond angles is 341° around O(8) and 335° around O(9).

The uncoordinated water molecule O(10) is situated between the neodymium malonate layers and forms the only inter layer hydrogen bonds. It is bonded to the water oxygens O(8), O(9) and O(7^{iv}) of one layer and to the carboxylic oxygen O(1^{vii}) of an adjacent layer (see Fig. 1). These four oxygens form a distorted tetrahedron around O(10) with the "tetrahedral" angles in the range 59 – 159°. The donor angle O(1^{vii}) – O(10) – O(7^{iv}) is 116°.

Acknowledgements. I am indebted to Professor Ido Leden and Drs. Jörgen Albertsson and Ingmar Grenthe for many valuable discussions. This work is part of a research project supported by the *Swedish Natural Science Research Council.*

REFERENCES

1. Grenthe, I., Gårdhammar, G. and Rundcrantz, E. *Acta Chem. Scand.* **23** (1969) 93.
2. Dellien, I. and Grenthe, I. *Acta Chem. Scand.* **25** (1971) 1387.
3. Hansson, E. *Acta Chem. Scand.* **24** (1970) 2969.
4. Hansson, E. *Acta Chem. Scand.* **26** (1972) 1337.
5. Hansson, E. *Acta Chem. Scand.* **27** (1973) 823 .
6. Butler, K. R. and Snow, M. R. *J. Chem. Soc.* **D1971** 550.
7. Azikov, B. S., Kharzeeva, S. E., Grankina, Z. A. and Serebrennikov, V. V. *Russ. J. Inorg. Chem.* **13** (1968) 954.
8. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1969, Vol. I.
9. Cruickshank, D. W. J. In Rollet, J. S. *Computing Methods in Crystallography*, Pergamon, Glasgow 1965, pp. 99 – 116.
10. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1968, Vol. III.
11. Cromer, D. T., Larsson, A. C. and Waber, J. T. *Acta Cryst.* **17** (1964) 1044.
12. Liminga, R. *Acta Chem. Scand.* **21** (1967) 1206.
13. Albertsson, J. *On the Stereochemistry of Ninecoordinate Lanthanoid Compounds*, Thesis, Lund 1972, p. 37.
14. Oskarsson, Å. *Acta Chem. Scand.* **25** (1971) 1206.
15. Sadikov, G. G., Kukina, G. A., Porai-Koshits, M. A. and Pospelova, L. A. *J. Struct. Chem.* **9** (1967) 128.
16. Sadikov, G. G., Kukina, G. A. and Porai-Koshits, M. A. *J. Struct. Chem.* **8** (1967) 492.
17. Sime, J. G., Speakman, J. C. and Parthaserathy, R. *J. Chem. Soc.* **A 1970** 1919.
18. Goedkoop, J. A. and MacGillavry, C. H. *Acta Cryst.* **10** (1957) 125.
19. Baur, W. H. *Acta Cryst.* **B 28** (1972) 1456.

Received March 15, 1973.