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Structural Studies on the Rare Earth Carboxlates

20. The Crystal and Molecular Structure of Mono-Aquo Hydroxo Malonato Scandium(III) Monohydrate

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The crystal and molecular structure of $Sc(OH)C_3H_2O_4.2H_2O$ has been determined from three-dimensional, photographic, X-ray intensity data. The crystals are monoclinic with $a=6.276(1)$ Å, $b=15.353(4)$ Å, $c=7.776(2)$ Å, $\beta=99.90(3)°$. The space group is $P2_1/n$ and $Z=4$. The structure is composed of infinite scandium-hydroxo-malonate chains running in the x-direction and linked to each other by hydrogen bonds. Within each chain the scandium ions are bonded to pairs by double oxygen bridges formed by the hydroxy ions, and the scandium pairs are in turn linked by carboxylate bridges Sc–OCO–Sc. The malonate ion forms a six membered chelate ring with scandium and is nonplanar with the carboxylate groups twisted about 40° in the same direction out of the carbon chain plane. The chelate ring has a boat conformation. Each scandium ion is octahedrally surrounded by two hydroxy oxygens, three carboxylate oxygens and one water oxygen. The Sc–O bond distances are in the range 2.05–2.12 Å.

The conformation of the malonate ion in lanthanoid malonate complexes has been studied in a series of X-ray investigations, involving the noniso-structural compounds $Nd_2mal_3.8H_2O$ (NDO),[1] $Nd_2mal_3.6H_2O$ (NDH),[2] and $Eu_2mal_3.8H_2O$ (EUM),[3] ($mal=CH_2(COO)_2$). Poor crystal quality prevented the study of a malonate $M_2mal_3.nH_2O$ formed by the smaller lanthanoid ions, and for that reason it has not been possible to investigate changes in the geometry of the malonate ion, attributable to the lanthanoid contraction.

Scandium(III) has a similar outer electron shell to the trivalent lanthanoid ions and a smaller ionic radius. Thus a possible influence of a change in size of the central ion on the malonate ligand might be revealed in a crystal structure analysis of a solid scandium malonate complex.

The compound chosen for this investigation is $Sc(OH)mal.2H_2O$ (SCM). A number of basic scandium dicarboxylates $Sc(OH)R(COO)_2.nH_2O$ have been reported.[4] Their crystal structures seem to be unknown and the determina-

tion of the function of the hydroxy ion in a compound of this type confers additional interest to the present investigation.

EXPERIMENTAL

Preparation and analysis. Scandium hydroxide (4 mmol) and malonic acid (6 mmol) were dissolved in 100 ml water. The pH of the resulting solution was about 3 and crystals of SCM were precipitated after standing at room temperature for several weeks. (Found: Sc 22.0; C 18.4; H 3.8. Calc. for $Sc(OH)C_3H_2O_4.2H_2O$ (200.2): Sc 22.5; C 18.0; H 3.6).

X-Ray diffraction work. A crystal of the approximate dimensions $0.10 \times 0.02 \times 0.04$ mm^3 mounted along the 0.10 mm edge was used in recording the layers $0kl - 5kl$, with the integrated Weissenberg multi-film technique. Ni-filtered Cu-radiation was used. The intensities of 779 independent reflexions were measured visually by comparison with a calibrated scale. These reflexions represent about 55 % of the possible number in the investigated region.

The intensities were corrected for Lorentz and polarisation effects. The linear absorption coefficient is 87 cm^{-1} but no corrections for absorption were applied.

The powder photograph was taken at room temperature in a Guinier-Hägg focusing camera with Cu$K\alpha$-radiation ($\lambda = 1.54178$ Å). Lead nitrate (cubic $a = 7.8568$ Å) was used as an internal standard.

UNIT CELL AND SPACE GROUP

The crystals of SCM are monoclinic with $a = 6.276(1)$ Å, $b = 15.353(4)$ Å, $c = 7.776(2)$ Å, and $\beta = 99.90(3)°$. $Z = 4$. The accurate values of the lattice parameters were determined from powder data by least squares refinement, as described before.[5] The observed values of $\sin^2\theta$ are compared with those calculated after the last cycle of refinement in Table 1.

The reflexions $h0l$, $h+l \neq 2n$ and $0k0$, $k \neq 2n$ are systematically absent. Thus the only possible space group is $P2_1/n$, the general position of which is fourfold: $\pm(x,y,z;\ \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The structure of SCM was determined by the heavy atom method. The position of the scandium ion was deduced from a three-dimensional Patterson synthesis and a following difference synthesis revealed the positions of the remaining ten non-hydrogen atoms.

The preliminary positional parameters, isotropic temperature factors and inter-layer scale factors were improved by full matrix least squares refinement. The discrepancy indices $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{\frac{1}{2}}$ converged to 0.095 and 0.124, respectively. The inter-layer scale factors were now fixed and further refinement with anisotropic thermal parameters for all non-hydrogen atoms resulted in $R = 0.081$ and $wR = 0.104$. The structure is described with the anisotropic model even though the intensity material is not very accurate and hence the thermal parameters may have little physical significance.

The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights, w, chosen according to Cruickshank.[6] An analysis of the weighting scheme used in the

Table 1. Powder data for $Sc(OH)(C_3H_2O_4).2H_2O$. 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 2 0	1006	1008	m	2 0 2	11977	12008	vw
0 1 1	1266	1266	vs	0 7 1	13356	13357	vw
1 1 0	1806	1806	vs	−3 0 1	13694	13701	s
0 2 1	2021	2022	vs	1 7 0	13893	13897	vvw
1 0 1	2134	2134	m	3 1 0	14240	14241	w
−1 1 1	2386	2386	w	−1 7 1	14488	14477	vw
−1 2 1	3148	3142	vvw	−3 2 1	14700	14709	vw
1 1 1	3255	3254	m	3 2 0	14987	14996	s
0 4 0	4021	4030	m	−3 1 2	15691	15693	vw
0 4 1	5055	5044	m	−3 3 1	15953	15968	m
0 2 2		5063		0 0 4	16254	16222	vw
1 4 0	5590	5585	w	3 3 0		16256	
2 0 0	6218	6217	m	0 8 1	17113	17135	vvw
0 3 2	6329	6323	w	1 8 0	17687	17676	vvw
−2 1 1	6624	6615	vs	3 4 0	18031	18019	vvw
−1 3 2	7013	7009	vw	0 3 4	18505	18489	vvw
2 2 0	7229	7225	w	−2 7 1	18707	18707	vvw
1 5 0	7863	7852	vvw	−3 4 2	19471	19472	vw
0 4 2	8090	8086	vvw	3 5 0	20287	20286	w
−2 3 1	8637	8631	vw	3 1 2	20912	20899	w
−1 4 2	8772	8773	vw	−3 3 3	21487	21477	vvw
2 2 1	9099	9106	m	2 8 0	22345	22339	vvw
0 1 3	9370	9377	w	1 8 2	22599	22599	vvw
0 2 3	10112	10133	vvw	3 5 1		22601	
−1 6 1	11205	11203	vvw	−3 6 1	22770	22770	vvw
				−4 1 1	24396	24399	w
				−3 1 4	25253	25257	w

last cycle of refinement is given in Table 2. In this cycle the shifts in all parameters were less than 1 % of their estimated standard deviations. The atomic scattering factors for the neutral atoms were for O and C taken from International Tables [7] and for Sc from Cromer *et al.*[8]

Table 2. Analysis of the weighting scheme $w = 1/(5.0 + |F_o| + 0.02|F_o|^2 + 0.005|F_o|^3)$. 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 $\sin \theta$	Number of reflexions	$\overline{w\Delta^2}$
0 – 7	77	0.79	0.00 – 0.37	71	2.38
7 – 9	78	0.86	0.37 – 0.47	68	1.12
9 – 10	78	0.96	0.47 – 0.54	72	0.92
10 – 12	78	1.38	0.54 – 0.59	61	1.03
12 – 14	78	1.10	0.59 – 0.64	62	0.62
14 – 16	78	1.05	0.64 – 0.68	51	0.74
16 – 19	78	0.81	0.68 – 0.71	47	1.00
19 – 24	78	0.92	0.71 – 0.74	46	0.75
24 – 35	78	0.65	0.74 – 0.77	39	0.51
35 – 130	78	1.49	0.77 – 0.80	40	0.93

Table 3. Atomic parameters with estimated standard deviations. The anisotropic thermal parameters, β_{ij}, have been obtained by using the expression $\exp[-(h^2\beta_{11}+2hk\beta_{12}+\ldots.)]$ and the root-mean-squares displacements along the principal axis of the thermal ellipsoids, R_i, have been calculated from the values of β_{ij}.

Atom	Group	$x\times10^4$	$y\times10^4$	$z\times10^4$	$\beta_{11}\times10^4$	$\beta_{22}\times10^4$	$\beta_{33}\times10^4$	$\beta_{12}\times10^4$	$\beta_{13}\times10^4$	$\beta_{23}\times10^4$	R_1/Å	R_2/Å	R_3/Å
Sc		391(2)	818(1)	6361(2)	154(6)	23(1)	115(3)	−3(1)	2(2)	−2(1)	0.185	0.164	0.174
O(1)	COO^-	3804(8)	741(3)	6701(7)	218(19)	32(2)	173(11)	−3(5)	1(11)	6(4)	0.236	0.194	0.202
O(2)	COO^-	7224(9)	1030(4)	6570(8)	194(22)	44(3)	202(13)	3(5)	4(12)	1(4)	0.245	0.193	0.229
O(3)	COO^-	2821(9)	3376(4)	5816(8)	316(18)	25(2)	191(13)	−16(5)	6(12)	7(4)	0.252	0.164	0.238
O(4)	COO^-	1052(9)	2131(4)	5978(9)	234(17)	29(2)	240(15)	−8(5)	6(12)	1(4)	0.267	0.182	0.213
O(5)	OH^-	265(8)	−533(3)	6264(7)	255(18)	29(2)	132(10)	−2(4)	3(10)	3(4)	0.223	0.180	0.200
O(6)	H_2O	832(9)	874(4)	9122(8)	264(19)	44(3)	135(10)	10(6)	3(10)	−12(5)	0.243	0.190	0.221
O(7)	H_2O	4169(11)	811(5)	11553(9)	341(24)	60(4)	211(15)	−18(7)	0(15)	24(6)	0.304	0.228	0.244
C(1)	COO^-	5255(12)	1222(5)	6247(10)	214(28)	34(3)	120(13)	1(7)	1(14)	−11(5)	0.221	0.173	0.201
C(2)	CH_2	4630(16)	2069(7)	5240(15)	349(33)	43(4)	266(26)	34(9)	11(23)	35(8)	0.316	0.196	0.234
C(3)	COO^-	2706(12)	2562(5)	5738(10)	279(26)	26(3)	131(13)	−9(6)	1(14)	12(5)	0.243	0.163	0.201

Table 4. Observed and calculated structure factors for the compound $Sc(OH)C_3H_2O_0.2H_2O$. In each group the running index l, $|F_o|$, and $|F_c|$ are given.

H= -5 K=-14	-2 9 8	0 10 9	3 18 19	H= -3 K= -3	-4 15 15	H= -1 K= 0	1 43 42
-2 6 7	-1 9 8	1 14 14	6 14 14	-5 10 11	-3 8 9	-7 26 29	2 11 12
0 10 10	0 11 11	2 11 10	5 6 7	-3 10 11	-2 38 37	-5 27 27	3 23 24
1 7 7	1 21 24	3 7 6		-2 15 16	-1 18 17	-3 88 104	4 7 8
2 13 13	2 9 8	4 19 17	H= -3 K=-12	-1 32 30	0 14 14	-1 12 11	5 26 26
4 10 13	4 11 10	5 9 10	-3 14 13	0 46 28	2 24 24	1 9 7	6 16 14
	5 20 20	6 11 9	-1 10 12	1 30 29	3 14 15	5 7 7	7 14 14
H= -5 K=-13	7 6 6	8 13 13	1 27 28	3 33 34	4 12 11	7 16 17	9 5 6
-2 10 12	8 8 7		3 14 14	4 23 20			
-1 6 6		H= -4 K= -5	5 19 19	5 25 25	H= -2 K= -8	H= -1 K= 1	H= -1 K= 9
0 9 9	H= -5 K= -1	-3 31 31		7 9 10	-6 8 8	-8 8 7	-5 18 17
2 7 8	-3 9 11	-2 8 7	H= -3 K=-11	9 11 10	-5 15 15	-7 11 11	-3 28 25
3 7 7	-2 20 18	0 5 5	-2 13 12		-4 21 20	-5 41 22	-1 38 33
4 13 11	0 9 10	1 47 45	0 18 17	H= -3 K= -2	-1 25 26	-4 19 22	0 16 13
	2 10 11	2 12 9	1 22 24	-4 44 42	0 40 41	-3 24 24	1 42 43
H= -5 K=-12	3 17 17	4 8 8	2 8 7	-3 34 32	1 8 7	-2 12 10	3 40 39
-3 13 14	4 11 12	5 28 27	3 22 21	-2 12 13	3 35 34	-1 53 62	4 20 20
-1 6 6	6 8 8		4 24 24	-1 4 4	4 16 15	0 27 28	5 26 26
1 15 17	8 7 8	H= -4 K= -4	5 9 9	0 95 87	5 8 8	1 12 10	7 21 17
3 6 6		-4 7 8	7 8 9	1 49 49	7 15 16	3 12 10	8 9 8
5 12 10	H= -5 K= 0	-2 6 6		2 17 17		6 10 12	
	-1 19 18	0 23 22	H= -3 K=-10	3 8 8	H= -2 K= -7	8 19 18	H= -1 K= 10
H= -5 K=-11	3 16 17	1 23 22	-4 20 20	4 17 16	-6 15 12		-8 7 7
-3 6 6	5 7 6	3 24 24	-3 18 19	5 14 13	-4 13 12	H= -1 K= 2	-4 10 11
-2 8 10		4 14 15	-2 16 17	6 12 13	-3 38 38	-8 7 6	-2 8 6
-1 11 12	H= -4 K=-16	6 15 16	-1 19 18	7 9 10	-2 23 23	-7 13 13	0 17 14
0 6 5	-1 10 11	7 15 16	0 26 28		0 28 23	-2 23 19	1 11 11
2 10 9	3 15 16	8 8 9	1 10 9	H= -3 K= -1	1 68 62	-1 44 43	2 25 25
3 8 9			2 28 28	-2 57 61	2 13 15	1 25 20	3 14 13
4 6 5	H= -4 K=-15	H= -4 K= -3	3 11 12	-1 17 16	5 15 14	2 13 9	6 21 21
6 5 6	0 12 14	-4 12 11	4 9 10	0 35 46	6 15 12	3 38 42	
	1 6 6	-2 18 18	6 19 17	1 10 11	6 12 12	5 15 14	H= -1 K= 11
H= -5 K=-10	3 4 7	0 16 17		2 44 41		6 15 15	-5 13 12
-4 13 13	4 13 11	1 12 11	H= -3 K= -9	3 21 18	H= -2 K= -6	7 16 17	-4 9 9
-2 12 13		2 15 13	-5 21 20	4 53 54	-6 13 13		-1 21 23
0 17 18	H= -4 K=-14	3 7 6	-3 38 41	5 14 15	-4 31 34	H= -1 K= 3	0 19 16
2 20 19	-2 6 6	4 19 15	0 12 12	7 12 11	0 60 59	-9 8 8	3 16 16
4 15 16	-1 7 9	6 14 15	2 6 5	8 18 20	1 5 6	-4 7 6	4 17 18
5 5 5	2 8 8	8 8 8	3 26 25		3 11 9	-3 27 25	8 9 8
6 9 8	3 7 8		4 8 7	H= -3 K= 0	4 34 35	-2 20 21	
	5 9 8	H= -4 K= -2	5 16 15	-3 55 55	5 14 14	-1 14 11	H= -1 K= 12
H= -5 K= -9		-3 15 15	7 10 12	-1 9 9	7 10 11	0 17 17	-7 17 15
-4 6 5	H= -4 K=-13	-2 6 6		3 23 21	8 13 15	1 69 69	-3 26 25
-3 7 8	-3 7 7	-1 13 13	H= -3 K= -8	5 39 37		2 29 29	1 20 21
-2 5 5	-2 15 15	0 6 6	-4 29 28	7 9 10	H= -2 K= -5	3 21 22	7 14 14
-1 11 12	-1 10 11	1 5 4	-3 28 31	9 7 7	-6 8 8	5 22 25	
0 16 17	0 8 9	3 20 19	-2 22 21		-3 26 29	7 9 9	H= -1 K= 13
2 9 9	1 10 10	4 22 22	0 47 49	H= -2 K=-18	-2 20 21	9 7 7	-5 11 11
3 12 11	2 12 11	5 12 12	1 35 33	0 12 11	-1 23 21		-3 13 12
4 12 12	4 6 7	6 13 14	2 33 31		1 12 13	H= -1 K= 4	-1 13 14
6 6 7	5 9 11	8 13 14	3 7 6	H= -2 K=-17	3 10 9	-8 7 6	0 25 23
7 13 13		9 7 7	4 17 17	1 12 13	5 20 21	-7 10 9	1 11 12
	H= -4 K=-12		5 14 14	-3 8 7	7 12 12	-4 16 18	2 9 9
H= -5 K= -8	-2 6 7	H= -4 K= -1	6 19 19	-2 13 13	9 9 9	-2 26 22	4 28 27
-4 13 13	0 8 7	-3 40 34		1 7 8		0 42 39	
-3 13 13	1 10 10	-2 19 16	H= -3 K= -7	2 10 12	H= -2 K= -4	1 23 22	H= -1 K= 14
0 18 18	2 14 12	-1 8 8	-6 16 17		-5 10 8	2 30 25	-6 10 9
1 19 18	4 7 8	0 18 21	-5 7 8	H= -2 K=-16	-4 9 10	4 8 8	-5 13 12
4 10 8	6 7 8	1 36 49	-4 10 11	-1 14 14	-3 6 6	5 12 12	-2 16 15
5 12 12		2 8 8	-2 43 44	1 10 9	-2 8 7	8 11 9	1 23 19
6 5 5	H= -4 K=-11	4 26 24	-1 16 17	3 11 12	-1 13 10		2 23 25
	-3 11 11	5 34 30	0 43 35	5 8 8	0 16 17	H= -1 K= 5	3 12 11
H= -5 K= -7	0 13 13	9 11 11	1 10 10		1 12 13	-3 8 9	5 16 15
-2 24 24	1 17 16		2 30 29	H= -2 K=-15	2 10 10	-2 16 16	6 20 17
0 5 6	4 13 13	H= -4 K= 0	3 22 20	-4 12 10	4 22 22	-1 20 22	
1 5 5	5 10 11	-2 22 21	4 48 42	-2 20 22	6 22 22	0 27 23	H= -1 K= 15
2 13 12		0 27 28	5 10 10	0 12 11	7 16 17	1 17 17	-5 17 16
4 9 9	H= -4 K=-10	2 34 34	6 7 8	2 15 16	8 10 10	2 14 13	-3 12 11
	-1 8 8	4 18 17	7 7 8		9 6 7	3 27 28	-2 13 14
H= -5 K= -6	2 9 9	6 17 16	8 15 17	H= -2 K=-14		4 18 18	-1 28 27
-3 18 16	5 7 6	R 11 12		-5 8 7	H= -2 K= -3	5 12 13	1 20 18
-1 5 5	6 5 5		H= -3 K= -6	-4 13 14	-4 14 14	8 13 12	3 25 25
1 25 21	7 14 14	H= -3 K=-18	-5 8 9	-3 8 8	-2 36 41		5 12 14
3 9 9		1 8 9	-3 45 46	0 24 22	-1 5 5	H= -1 K= 6	
4 6 7	H= -4 K= -9		-1 11 10	1 8 9	1 40 37	-7 19 21	H= -1 K= 16
5 19 16	-4 16 14	H= -3 K=-17	0 11 10	3 21 21	2 10 11	-5 10 9	-6 10 11
7 6 5	0 17 15	-2 8 8	1 73 59		3 28 26	-3 39 40	-3 10 10
	2 7 6	-1 8 9	2 16 16	H= -2 K=-13	6 12 11	-1 22 25	-2 14 16
H= -5 K= -5	4 14 14	0 7 7	3 6 6	-4 9 9		0 33 30	0 16 18
-3 6 6	5 7 9	1 7 8	5 26 21	-3 18 20	H= -2 K= -2	1 35 36	2 15 15
-2 12 13	6 7 8		7 9 9	1 19 19	-5 14 13	2 6 6	
-1 7 7		H= -3 K=-16	9 5 5	5 9 9	-4 28 30	3 28 31	H= -1 K= 17
0 8 7	H= -4 K= -8	-3 8 8		6 9 11	-3 15 15	4 11 12	-6 11 11
2 12 10	-5 12 14	-2 12 11	H= -3 K= -5		-2 10 10	5 12 13	-1 8 8
4 6 7	-3 8 9	0 12 14	-5 9 9	H= -2 K=-12	-1 36 42	7 20 20	0 10 12
6 7 7	-2 8 8	1 6 6	-4 8 7	-6 12 11	0 57 57		3 10 10
8 5 5	-1 24 22	2 15 15	-3 8 9	2 20 20	1 10 12	H= -1 K= 7	4 12 11
	2 13 12	4 7 6	-2 17 19	4 18 17	2 19 13	-8 9 10	
H= -5 K= -4	3 23 22		-1 15 18		3 65 68	-6 11 10	H= -1 K= 18
-4 15 15	6 7 7	H= -3 K=-15	0 53 47	H= -2 K=-11	4 35 35	-4 35 34	-3 10 9
-2 11 10	7 7 9	-1 22 22	2 18 18	-4 9 10	7 21 21	-3 23 25	1 9 8
0 18 17	9 7 8	3 15 16	3 12 10	-3 10 11	8 9 9	-2 26 28	3 10 8
1 6 5		5 7 8	4 58 53	-1 9 9		-1 9 11	
2 15 14	H= -4 K= -7		5 7 8	0 12 13	H= -2 K= -1	0 52 50	H= -1 K= 19
3 6 6	-4 9 8	H= -3 K=-14	8 17 18	1 9 8	-4 26 26	1 40 37	0 5 6
4 15 15	-3 20 20	-4 18 17		4 24 22	-3 56 57	2 35 38	1 5 6
5 8 7	-2 20 20	-3 15 16	H= -3 K= -4	6 8 9	-2 7 6	3 10 10	
7 6 5	-1 15 14	-2 14 15	-5 7 5		0 13 15	4 43 47	H= 0 K= 0
	0 13 13	-1 8 7	-4 22 24	H= -2 K=-10	1 86 84	5 11 11	2 19 17
H= -5 K= -3	1 34 34	0 21 23	-3 14 13	-5 12 11	2 6 3	6 13 12	4 101 114
-3 8 6	2 16 17	1 12 11	-2 12 13	-1 14 14	3 12 11	8 16 17	6 9 8
-2 9 9	3 16 15	2 17 16	0 54 33	0 18 17	5 32 34		8 16 14
0 8 8	4 13 9	4 12 11	2 62 57	1 17 16	9 9 10	H= -1 K= 8	
2 8 8	5 22 20	6 9 9	3 7 6	3 14 14		-7 12 12	H= 0 K= 1
3 12 10	6 8 8		4 20 19	5 12 10	H= -2 K= 0	-6 23 21	1 48 61
4 5 6		H= -3 K=-13	5 8 8	6 8 8	-4 37 39	-4 16 16	2 96 117
7 9 9	H= -4 K= -6	-2 18 21	6 21 22	7 8 9	-2 8 8	-3 35 32	3 62 74
	-3 8 10	0 14 15			4 50 46	-2 27 29	6 11 13
H= -5 K= -2	-2 11 11	1 18 18		H= -2 K= -9	8 23 25	-1 9 8	7 28 30
-3 10 9	-1 17 16	2 17 15		-6 16 16		0 35 35	

Table 4. Continued.

H= 0 K= 2			H= 0 K= 4			8 8 8			6 18 15			2 45 44			H= 0 K= 12			H= 0 K= 15			H= 0 K= 18		
0	44	39	0	75	72				7 18 16			4 28 28			8 38 38			1 15 14			0 11 11		
1	59	81	1	41	49	H= 0 K= 6			8 9 8			6 20 18			4 21 21			2 29 26					
2	42	50	2	23	24	0 130 134						8 17 14						4 9 7					
3	33	36	3	24	23	1 13 13			H= 0 K= 8						H= 0 K= 13			6 14 12					
4	33	39	4	35	37	2 17 21			0 58 54			H= 0 K= 10			2 14 13								
5	34	33	5	20	19	4 59 60			1 57 65			0 25 22			3 14 15			H= 0 K= 16					
6	22	20	6	13	11	5 13 13			3 63 50			1 14 16			7 11 10			0 11 10					
8	10	11	8	9	8	6 19 16			4 26 23			4 9 8						1 21 19					
9	10	10				8 9 10			5 20 19			5 17 14			H= 0 K= 14			3 19 16					
			H= 0 K= 5						6 10 10			6 10 9			0 21 21			5 10 8					
H= 0 K= 3			1 11 16			1 52 55			7 10 7						1 16 14								
2 53 61			2 18 18			2 46 45			8 8 7			H= 0 K= 11			4 15 12			H= 0 K= 17					
4 58 66			5 50 54			5 35 35						2 16 14			5 10 14			1 9 8					
6 26 25			4 15 17			6 19 20			H= 0 K= 9			5 16 14						2 12 10					
8 22 20			7 21 20			5 10 9			1 17 17			7 10 10						4 8 6					

The final atomic parameters are given in Table 3. The electron density maps of a different synthesis based on these parameters and calculated for F_o with $\sin\theta/\lambda \leq 0.5$ showed a broad maximum, 0.6 e/Å^3, in the region between the expected positions of the methylene hydrogens. Maxima of this height were also found in the region between the presumably hydrogen bonded oxygens O(5) and O(3), and O(6) and O(7). Attempts to refine the positions of these four hydrogen atoms failed however. All other peaks were less than 0.6 e/Å^3 and were judged as spurious.

The observed values of F_o are compared to those calculated in the last cycle of refinement in Table 4.

All computations were performed on the UNIVAC 1108 computer at Lund, Sweden, using the programmes DRF, LALS, DISTAN, PLANE, CELSIUS and ORTEP.[9]

DESCRIPTION OF THE STRUCTURE

The superscripts (i) – (x) are used to indicate the following equivalent positions in the structure

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

where x,y,z are the atomic coordinates given in Table 3.

The scandium ion is octahedrally surrounded by three carboxylate oxygens O(1), O(2), and O(3), contributed by two malonate ions, two hydroxy oxygens O(5), and one water oxygen O(6) as illustrated in Fig. 1. The octahedra are connected in pairs by the sharing of the edge O(5) – O(5). The resulting Sc···Sc distance is 3.27 Å. Carboxylate bridges like Sc – O(1)C(1)O(2) – Sc^x link the octahedra in infinite chains around the lines $y=0$, $z=1/2$ and $y=1/2$, $z=0$. The malonate ion forms a six-membered chelate ring with scandium and has one uncoordinated oxygen O(3) which points away from the chain in the y-direction.

The chains are hydrogen bonded to each other. This feature is shown in Fig. 2. The hydrogen bonds between chains at the same y-level are formed

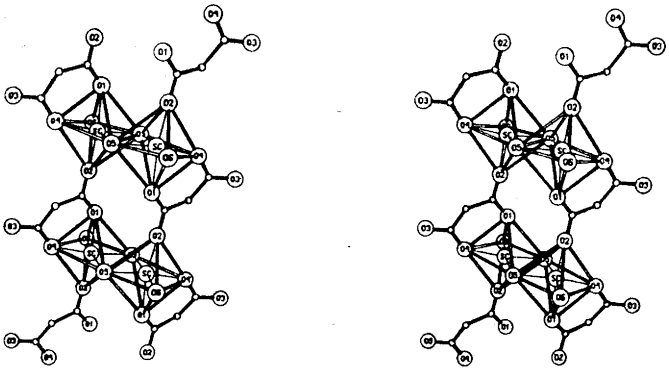

Fig. 1. A stereoscopic pair of drawings showing part of an infinite scandium-malonate chain. The Sc – O bonds are indicated by single lines, bonds within the malonate ions are filled and the edges of the octahedra are open.

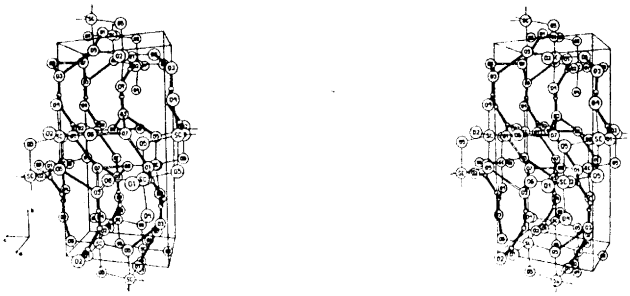

Fig. 2. A stereoscopic pair of drawings illustrating the hydrogen bond system and the packing of the scandium malonate chains. Hydrogen bonds are open and other bonds are indicated as in Fig. 1.

via the uncoordinated water molecule O(7) and those between chains at adjacent y-levels *via* the uncoordinated carboxylate oxygen O(3). Within the same y-level the chains are closely packed; the shortest inter-chain contact is $O(6^{ix})\cdots O(6^{vii})$, 3.27 Å. Furthermore the oxygens O(3) and O(7) are situated between these chains resulting in a crowding of oxygens around $y=0$, $z=0$ and $y=1/2$, $z=1/2$.

The coordination around scandium. The dimensions of the coordination polyhedron are given in Table 5 A. The Sc – O bond distances range from 2.05 to 2.12 Å with the average 2.08 Å. This value is within 0.02 Å equal to that reported for sixcoordinated scandium in $Sc(HCOO)_3$.[10] It may also be compared to the average Sc – O bond distance, 2.23 Å, found in $Sc_2(C_2O_4)_3.6H_2O$,[11] where the coordination number of scandium is eight. The difference in ionic radius of scandium(III) between eight and six coordination is 0.14 Å [12] and thus the agreement is good. These two structures seem to be the only scandium carboxylate structures previously reported.

The octahedron is somewhat distorted, with O – Sc – O bond angles in the range 76° – 98°. The distance between the bridging oxygens O(5)···O(5^{ii}) is 2.54 Å. All other O – O contact distances are within 0.21 Å from the average, 2.95 Å. Thus the malonate ion, with the bite O(1)···O(4), 2.74 Å, spans the next shortest edge of the distorted octahedron.

The chelate ring has a boat conformation; the carboxylate atoms C(1), O(1), C(3), and O(4) are coplanar within 0.04 Å and the scandium ion and the methylene carbon are situated at the same side of this plane (Table 6). This conformation is almost invariably found for six-membered malonate chelate rings.[3]

The malonate ion. The bond distances and angles within the malonate ion are given in Table 5B, and are also included in Fig. 3. They are in agreement with those found in other malonate structures.[1]

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

A. The coordination polyhedron

Sc – O(1)	2.116(5)	O(1) – Sc – O(6)	85.6(2)
Sc – O(2^{i})	2.048(6)	O(2^{i}) – Sc – O(4)	94.4(2)
Sc – O(4)	2.090(6)	O(2^{i}) – Sc – O(5)	95.5(2)
Sc – O(5)	2.076(5)	O(2^{i}) – Sc – O(5^{ii})	94.6(2)
Sc – O(5^{ii})	2.059(5)	O(2^{i}) – Sc – O(6)	82.7(2)
Sc – O(6)	2.119(6)	O(4) – Sc – O(5^{ii})	94.3(2)
O(1) – Sc – O(4)	81.4(2)	O(4) – Sc – O(6)	96.3(2)
O(1) – Sc – O(5^{ii})	97.9(2)	O(5) – Sc – O(6)	94.3(2)

B. The malonate ion

C(1) – C(2)	1.533(13)	C(1) – C(2) – C(3)	115.7(8)
C(2) – C(3)	1.531(13)	O(1) – C(1) – O(2)	122.5(7)
C(1) – O(1)	1.270(9)	O(1) – C(1) – C(2)	120.2(7)
C(1) – O(2)	1.253(10)	O(2) – C(1) – C(2)	117.3(7)
C(3) – O(3)	1.253(10)	O(3) – C(3) – O(4)	123.6(7)
C(3) – O(4)	1.271(10)	O(3) – C(3) – C(2)	117.7(7)
O(1) – O(4)	2.743(8)	O(4) – C(3) – C(2)	118.6(7)
Dihedral angles:			
C(3) – C(2) – C(1) – O(1)	35.3	C(1) – C(2) – C(3) – O(3)	140.1
C(3) – C(2) – C(1) – O(2)	145.6	C(1) – C(2) – C(3) – O(4)	42.8

C. Possible hydrogen bonds

O(5) – O(3^{iii})	2.910(8)	O(1^{v}) – O(7) – O(3^{vi})	98.9(3)
O(6) – O(3^{iv})	2.736(8)	O(3^{iv}) – O(6) – O(7)	101.8(3)
O(6) – O(7)	2.570(9)	O(6) – O(7) – O(3^{vi})	115.6(3)
O(7) – O(1^{v})	2.922)9)	O(7) – O(3^{vi}) – O(6^{x})	125.3(3)
O(7) – O(3^{vi})	2.755(9)		
Sum of bond angles around:	O(5)	356.4	
	O(6)	357.2	
	O(7)	341.9	

Table 6. Deviations in Å, from the least-squares planes through the C–COO-groups and through the carboxylate atoms of the chelate ring. In each case the atoms defining the plane are given above the asterisk.

The C–COO-groups				The chelate ring	
Atom	Distance	Atom	Distance	Atom	Distance
C(2)	0.001	C(2)	0.004	C(1)	0.037
C(1)	−0.004	C(3)	−0.015	O(1)	−0.035
O(1)	0.002	O(3)	0.005	C(3)	−0.037
O(2)	0.002	O(4)	0.005	O(4)	0.035
*		*		*	
Sc	0.039	Sc	−0.321	Sc	0.324
Sc^{x}	0.426			C(2)	0.447

The two C–COO groups are planar within the limits of errors (Table 6). The dihedral angles included in Table 5B and in Fig. 3 indicate that the carboxylate groups are twisted in the same direction out of the carbon chain plane by about 40°. Similar twists have been found in all previously studied malonate chelates.

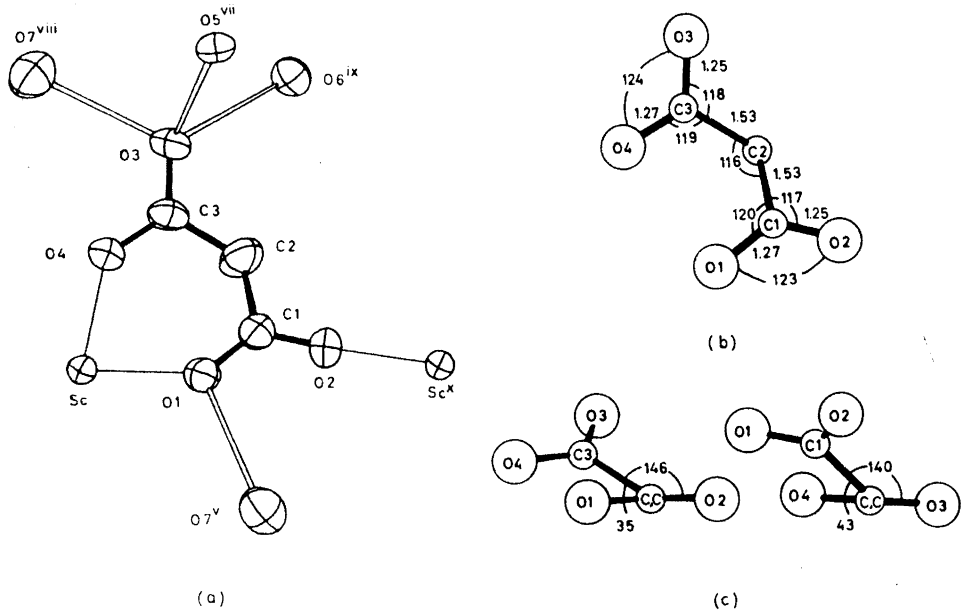

Fig. 3. (a) The malonate ion with its immediate surroundings. The "thermal ellipsoids" are scaled to include 50 % of the probability distribution. (b) Bond distances (Å) and angles (°) within the malonate ion. (c) Projections of the malonate ion along each of its C–C bonds. The angles included are the dihedral angles C–C–C–O.

The bonding situation of the malonate ion is approximately the same as found for the malonate ions forming six-membered chelate rings in NDO [1] and NDH,[2] *i.e.* one nonchelating oxygen is bonded to an adjacent metal ion and the other is hydrogen bonded in the structure. These three malonate ions are compared in Table 7. The ligand bite seems to be somewhat shorter in the sixcoordinated scandium complex than in the ninecoordinated neodymium complexes but it must be concluded that the influence of the change in size of the central ion is small.

Table 7. A comparison of the malonate ions forming six-membered chelate rings with neodymium(III) (NDO, NDH) and with scandium(III) (SCM). ϕ_1 is the angle between the plane of the bridging carboxylate group and the carbon chain plane, and ϕ_2 is the corresponding angle for the hydrogen bonded carboxylate group (see text).

	NDO	NDH	SCM
ϕ_1/°	41	34	35
ϕ_2/°	51	41	51
bite/Å	2.80(2)	2.83(2)	2.743(8)

The possible hydrogen bonds. The O – O distances suitable for hydrogen bond formation are given in Table 5C. They are selected by the same criteria as used before.[1]

Judging from these distances the scandium-malonate chains are held together by hydrogen bonds *via* the uncoordinated oxygens O(7) and O(3), as illustrated in Fig. 2. The water molecules O(6), coordinated to the scandium ions of one chain, form together with water molecules O(7) and carboxylate oxygens O(3), a hydrogen bonded chain with the sequence –O(6)–O(7)–O(3)–O(6)– and running in the x-direction. The O – O bond distances in this chain are 2.57 – 2.76 Å. Weaker hydrogen bonds, 2.9 Å, link O(3) and O(7) to the hydroxy oxygens O(5) and carboxylate oxygens O(1) of an adjacent scandium malonate chain.

The atoms O(5^{vi}), O(6^{ix}), O(7^{x}), and C(3) form a distorted tetrahedron around O(3) with "tetrahedral" angles in the range 80 – 129°. The sum of the three bond angles around the hydrogen bond donors O(5), O(6), and O(7) are given in Table 5C, which also includes the donor angles of O(6) and O(7) and the O – O – O angles within the hydrogen bonded chain.

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