

Structural Studies on the Rare Earth Carboxylates

5. The Crystal and Molecular Structure of Neodymium(III) Oxalate 10.5-Hydrate

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The crystal and molecular structure of the compound, $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10.5\text{H}_2\text{O}$, has been determined from three-dimensional X-ray intensity data. The crystals are monoclinic with the space group $P2_1/c$ and have the lattice parameters $a=11.678(2)$ Å, $b=9.652(2)$ Å, $c=10.277(2)$ Å and $\beta=118.92(2)^\circ$, $Z=2$. The crystal structure is composed of infinite neodymium oxalate networks in layers perpendicular to b . Water molecules are situated between these layers. One third of the water molecules are not located yet but are assumed to be occluded into the fairly large free spaces in the structure. The neodymium atom is coordinated by six carboxylic and three water oxygen atoms which form a coordination polyhedron based on a distorted trigonal prism. Each oxalate ion is coordinated to two neodymium atoms, forming two chelates.

The lanthanoid elements all form hydrated oxalates of the composition $\text{M}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ ($\text{M}=\text{lanthanoid}$). The number n seems to be dependent on the mode of preparation. It is commonly close to ten for the compounds with $\text{M}=\text{La}-\text{Ho}$, while a variety of values has been obtained for the last four members of the series.

The X-ray powder diffraction pattern of the compounds are similar through the series up to and including the holmium one. The compounds of Er and Tm with $n \approx 10$ show one pattern and those of Yb and Lu with $n \approx 7$ another both quite different from the pattern exhibited by the solids in the beginning of the series.

None of these lanthanoid oxalate structures were known when this investigation started. A preliminary report on the structure of $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ has been published.¹ During the continued work on this structure Ollendorff and Weigel² have published unit cell dimensions and space groups of all the compounds from $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ to $\text{Dy}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$; the preliminary structures for the first four compounds were also reported.

This paper will give a detailed report on the crystal and molecular structure of the compound $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10.5\text{H}_2\text{O}$, neodymium(III) oxalate 10.5-hydrate.

EXPERIMENTAL

Preparation and analysis. Single crystals of the compound, $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10.5\text{H}_2\text{O}$ were precipitated from a solution of neodymium sulphate in a mixture of sulphuric and oxalic acid according to Weigel *et al.*³ Analyses: (Found: Nd 38.9; C 9.8; H 2.2; H_2O 25.7. Calc. for $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10.5\text{H}_2\text{O}$ (741.8): Nd 38.9; C 9.7; H 2.8; H_2O 25.5).

Single crystal work. The method of preparation results in crystals which are tabular (010). A single crystal of the approximate dimensions $0.15 \times 0.05 \times 0.10 \text{ mm}^3$, mounted along the *b*-axis, was used to record the layers $h0l-h8l$. Non-integrated Weissenberg photographs were taken with $\text{MoK}\alpha$ -radiation. For each layer three films separated by tin foils were exposed.

The intensities of 1357 independent reflexions were measured visually by comparison with a calibrated scale. 1258 reflexions were within the copper sphere, representing only 51 % of the possible number. This low value is due mainly to the position of the heavy neodymium atom (see p. 2972).

The linear absorption coefficient, μ , is 31 cm^{-1} . No absorption correction was applied to the intensity data. Corrections for the Lorentz and polarisation effects were made using the data reduction and Fourier calculation program DRF.⁴ All calculations were performed on the CD 3600 computer at Uppsala, Sweden.

UNIT CELL AND SPACE GROUP

The compound, $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10.5\text{H}_2\text{O}$, crystallizes in the monoclinic system. The unit cell dimensions have been determined previously by Jenkins *et al.*⁵ and by Weigel and Ollendorff.⁶ Jenkins *et al.* chose a unit cell whose outlines correspond with the shape of the crystal, while Weigel and Ollendorff chose the completely reduced cell, where the *a*-axis is not parallel with any of the crystal edges. A comparison between the cells is given by Weigel and Ollendorff. The cell of Jenkins *et al.* has been used for $\text{M}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ ($\text{M} = \text{La},^{5,7} \text{Nd},^{5,8} \text{Pm},^3 \text{Sm},^3 \text{Gd}^5$) by several authors and is also chosen in this work. The indexes obtained by using the different cells are related by the matrix $\text{A} = (-1, 0, -1 / 0, -1, 0 / 0, 0, 1)$; $\text{A} = \text{A}^*$.

The values of the lattice parameters obtained from powder data, are given below together with other crystal data.

$$\begin{array}{ll} a = 11.678(2) \text{ \AA} & D_m = 2.43 \text{ gcm}^{-3} \\ b = 9.652(2) \text{ \AA} & D_x = 2.43 \text{ gcm}^{-3} \\ c = 10.277(2) \text{ \AA} & Z = 2 \\ \beta = 118.92(2)^\circ & \mu = 31 \text{ cm}^{-1} \\ V = 1013(1) \text{ \AA}^3 & \end{array}$$

The results are in good agreement with those previously reported. The powder photographs were taken at room temperature in a Guinier focusing camera with $\text{CuK}\alpha$ -radiation, $\lambda = 1.54178 \text{ \AA}$, as will be described more fully in a subsequent paper in this series. The density of the crystals D_m was determined by the displacement method.

All reflexions $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$ are absent. Hence the only possible space group is $P2_1/c$ (No. 14),⁸ the general position of which is fourfold: $\pm(x, y, z; x, 1/2 - y, 1/2 + z)$.

Furthermore most of the reflexions with $k+l \neq 2n$ are absent for $k=1$ and those with $k+l \neq 2n+1$ are absent or very weak for $k=5$ and 6 and to a certain extent even for $k=4$ and 7. In the space group $P2_1/c$ the contribution to the structure factors of an atom with $y=0$ is zero when $k+l \neq 2n$ and so is that of an atom with $y=1/4 \cdot k$ when $k+l=2n+1$. The absences found thus indicate that for the heavy neodymium atom $y \approx 0$ and $1/4 \times 6 < y < 1/4 \times 5$ i.e. $0.042 < y < 0.050$. The y -value obtained in the final refinement is 0.046.

REFINEMENT OF THE STRUCTURE

The positional parameters of the neodymium atom, the carbon and oxygen atoms of the ligands and the oxygen atoms of the coordinated water molecules were approximately known from the preliminary work.¹ These parameters were refined together with the isotropic temperature factors of the atoms and the inter layer scale factors using the full matrix, least squares program LALS.⁴ After three cycles the value of $R = \sum ||F_o| - |F_c|| / \sum |F_c|$ had decreased from 0.145 to 0.098.

The function minimized was $w(|F_o| - |F_c|)^2$ with weights, w , chosen according to Cruickshank.⁹ The atomic scattering factors for the neutral atoms were taken from *International Tables for X-ray Crystallography*¹⁰ (oxygen and carbon) and from Cromer *et al.*¹¹ (neodymium).

A three-dimensional difference synthesis calculated at this stage using the program DRF was expected to reveal the positions of the uncoordinated oxygen atoms but showed only small peaks. The highest one, about $4.5 \text{ e}/\text{\AA}^3$, was situated at the position of the neodymium atom. Two peaks, about $3 \text{ e}/\text{\AA}^3$, situated at (0.56, 0.30, 0.24) and (0.40, 0.46, 0.38) were the only ones at reasonable distances from the other atoms. These are approximately the same positions as Ollendorff and Weigel² give for fractions of oxygen atoms. Refinement with one oxygen atom in each position was not possible. With the occupation number 0.5 the refinement was successful for the position (0.56, 0.30, 0.24) but not for (0.40, 0.46, 0.38). One half of an oxygen atom in the first position was included in the following refinement. The occupation number could not be refined by the program used but the reasonable temperature factor of O(10) indicates that the value 0.5 is not too far from the correct value. No attempt was made to find positions of oxygen atoms with occupation numbers less than 0.5 or to locate hydrogen atoms.

The coordinates and isotropic temperature factors of the atoms located and the inter layer scale factors were further improved by several cycles of least squares refinement. After the last cycle, when the shifts of all parameters were less than 1 % of their estimated standard deviations, the value of R was 0.095 and that of $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ was 0.120.

Because of the unequal electron density distribution around the $4.5 \text{ e}/\text{\AA}^3$ peak at the position of the neodymium atom, further refinement using anisotropic thermal parameters for this atom was performed. After three cycles the shifts of all parameters were less than 1 % of their estimated standard deviations. The value of R was still 0.095 while that of wR had decreased to 0.118.

A final difference synthesis showed a smoother electron density distribution around the peak at the position of the neodymium atom, which had decreased to about $4 \text{ e}/\text{\AA}^3$. Besides this peak two peaks of about $3 \text{ e}/\text{\AA}^3$ were detected, one at (0.40, 0.46, 0.38) and the other at about 1 \AA from O(3). All other peaks were small, $1-2 \text{ e}/\text{\AA}^3$, over a slowly varying background.

The approximate constancy of the average values of $w(|F_o| - |F_c|)^2$ in different $|F_o|$ and $\sin \theta$ intervals shows that the weighting scheme used is reasonable (Table 1). Since no systematic differences between $|F_o|$ and $|F_c|$ of the strong low-angle reflexions were detected, no correction for extinction was applied to the values of $|F_o|$.

Table 1. Analysis of the weighting scheme $w=1/(50+|F_o|+0.01|F_c|^2+0.0001|F_o|^3)$. The averages, $w\Delta^2$, 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—30	135	0.96	0.00—0.21	154	1.47
30—36	136	0.97	0.21—0.26	158	1.00
36—41	135	1.03	0.26—0.30	165	1.29
41—47	134	1.26	0.30—0.33	142	0.97
47—52	135	0.93	0.33—0.36	117	0.76
52—59	134	0.68	0.36—0.38	105	0.82
59—71	135	0.80	0.38—0.40	91	0.92
71—83	136	0.73	0.40—0.42	75	0.80
83—107	136	1.11	0.42—0.43	67	1.30
107—223	135	1.53	0.43—0.45	54	0.67

The magnitudes of the observed and finally calculated structure factors are listed in Table 2. The ultimate atomic coordinates and thermal parameters with their estimated standard deviations are given in Table 3. The atomic parameters found are within the limits of errors compatible with those given by Ollendorff and Weigel. Since different unit cells are used the coordinates have to be related to the same unit cell before comparison. The transformation is given by $(x',y',z')=(-1/2,1,0)+(1,0,0/0,-1,0/1,0,-1)(x,y,z)$ where (x,y,z) refers to the unit cell used in the present work. Selected values of interatomic distances and angles, calculated from the refined unit cell dimensions and atomic coordinates and their estimated standard deviations using the program DISTAN⁴ are collected in Tables 4, 5, and 7.

DESCRIPTION OF THE STRUCTURE

The superscripts (i)–(xi) are used to indicate the following equivalent sites in the structure,

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

Table 2. Observed and calculated structure factors.

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	
3	0	0	165	-176	11	1	1	57	-58	4	2	1	26	-24	0	2	8	53	55	-11	3	4	64	-71	-6	4	1	122	-126	
5	0	0	216	216	9	1	1	85	-88	4	2	1	133	115	-1	2	8	30	-31	-12	3	4	44	-51	-8	4	1	145	113	
6	0	0	121	127	8	1	1	51	53	-4	2	1	56	60	-2	2	8	120	-112	-14	3	4	49	44	-9	4	1	90	95	
8	0	0	98	-104	6	1	1	116	-125	-5	2	1	76	-77	-3	2	8	29	-27	9	3	5	46	-41	-10	4	1	20	-21	
9	0	0	55	-54	-7	1	1	40	-44	-6	2	1	77	-78	-4	2	8	87	82	6	3	5	45	42	-11	4	1	56	-64	
10	0	0	172	86	4	1	1	142	152	-7	2	1	126	-120	-5	2	8	87	87	4	3	5	74	-70	-12	4	1	15	-17	
11	0	0	51	53	3	1	1	149	150	-8	2	1	33	43	-6	2	8	32	-29	3	3	5	66	-59	-11	4	1	29	34	
13	0	0	52	-58	2	1	1	30	-29	-9	2	1	65	65	-7	2	8	116	-102	2	3	5	31	35	-14	4	1	40	48	
14	0	0	46	-31	-3	1	1	66	42	-11	2	1	44	-46	-8	2	8	77	-68	1	3	5	87	81	-16	4	1	28	-23	
16	0	0	47	37	-4	1	1	180	-170	-14	2	1	37	27	-9	2	8	44	44	-1	3	5	82	-77	-10	4	2	23	-21	
12	0	0	65	58	-5	1	1	182	-158	12	2	2	48	50	-10	2	8	73	72	-2	3	5	87	-83	9	4	2	30	-34	
6	0	2	52	-51	-9	1	1	65	-66	10	2	2	43	-44	-12	2	8	56	-63	-4	3	5	96	99	7	4	2	41	38	
9	0	2	80	-82	-10	1	1	159	-118	-15	2	2	74	-75	-13	2	8	54	-54	-5	3	5	32	43	6	4	2	23	22	
7	0	2	101	112	-12	1	1	57	62	7	2	2	90	84	-15	2	8	57	50	-6	3	5	67	-75	5	4	2	19	-28	
6	0	2	102	106	-15	1	1	56	46	6	2	2	68	66	3	2	9	55	35	-7	3	5	115	-109	4	4	2	40	-44	
5	0	2	71	-77	5	1	2	36	42	5	2	2	23	-25	0	2	9	50	50	-9	3	5	11	75	3	2	11	-41		
4	0	2	172	-159	2	1	2	36	39	4	2	2	119	-104	-2	2	9	59	58	-10	3	5	46	49	2	2	2	86	79	
2	0	2	201	206	1	1	2	33	38	3	2	2	64	-61	-3	2	9	37	39	-12	3	5	57	-61	1	4	2	42	41	
1	0	2	193	173	-5	1	2	135	158	2	2	2	111	111	-5	2	9	62	-63	-15	3	5	47	41	0	4	2	45	-39	
-3	0	2	141	137	-5	1	2	111	119	-2	2	2	166	135	-6	2	9	34	-28	-6	3	6	6	3	6	6	4	2	107	-94
-4	0	2	178	176	-10	1	2	41	36	-3	2	2	98	-105	-7	2	9	34	33	5	3	6	47	45	-2	4	2	57	-58	
-5	0	2	57	-52	10	1	3	64	67	-4	2	2	89	93	-8	2	9	49	45	4	3	6	38	33	-3	4	2	59	60	
-6	0	2	178	-167	8	1	3	74	-77	-7	2	2	126	-109	-11	2	9	47	-49	-10	3	6	60	57	-4	4	2	75	65	
-7	0	2	106	-109	8	1	3	90	-91	-7	2	2	98	-105	-11	2	9	32	-35	2	3	6	40	-42	4	4	2	68	-61	
-8	0	2	76	66	-8	1	3	127	135	-8	2	2	25	27	2	2	10	55	42	1	3	6	70	-71	-7	4	2	68	-71	
-9	0	2	99	86	5	1	3	75	89	-9	2	2	81	80	0	2	10	55	-42	0	3	6	65	-65	-9	4	2	20	32	
-11	0	2	83	-86	5	1	3	83	-86	5	1	3	73	-77	-1	2	10	35	-44	4	3	6	89	76	-4	4	2	23	-23	
-12	0	2	100	-86	2	1	3	203	-191	-12	2	2	68	-64	-3	2	10	54	59	-3	3	6	48	47	-12	4	2	24	-29	
-14	0	2	57	57	1	1	3	40	-35	-14	2	2	52	49	-5	2	10	56	-57	-4	3	6	57	-55	14	3	3	34	55	
-11	0	2	60	-61	1	1	3	42	-45	-12	2	2	39	30	-5	2	10	79	-76	-7	3	6	97	-92	12	3	3	31	-32	
9	0	4	49	41	-1	1	3	124	108	11	2	3	34	-31	-8	2	10	59	60	-5	3	6	71	65	6	4	2	36	-20	
8	0	4	51	54	-2	1	3	57	-58	9	2	3	36	42	-9	2	10	48	59	-8	3	6	77	76	9	4	3	73	77	
6	0	4	103	-108	-3	1	3	157	-148	7	2	3	29	-23	-10	2	10	32	-26	-9	3	6	41	-45	8	4	3	25	31	
4	0	4	94	-94	-5	1	3	94	-100	6	2	3	36	-39	-11	2	10	35	-36	-10	3	6	41	-45	8	4	3	25	31	
4	0	4	94	94	-5	1	3	88	93	6	2	3	36	-39	-11	2	10	54	56	-13	3	6	46	50	6	4	3	119	-103	
3	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-3	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-4	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-5	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-6	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-7	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-8	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-9	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-10	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-11	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-12	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-13	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-14	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-15	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-16	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-17	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-18	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-19	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-20	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-21	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-22	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-23	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-24	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
-25	0	4	92	94	-6	1	3	114	105	4	2	3	71	64	-14	2	10	51	52	-15	3	6	47	48	4	4	3	150	115	
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Table 3. Atomic parameters with estimated standard deviations for the compound $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10.5\text{H}_2\text{O}$. The space group is $P2_1/c$ (No. 14). The occupation number of the position O(10) is 0.5 and 1/3 of the water oxygen atoms are not located. B denotes the isotropic temperature factor.

Atom	Group	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$B/\text{\AA}^2$
Nd		1898 (1)	453 (1)	3588 (1)	^a
O(1)	—COO [−]	3931(14)	− 688(17)	5555(16)	1.7(2)
O(2)	—COO [−]	3927(16)	1048(19)	3553(18)	2.2(3)
O(3)	—COO [−]	1267(18)	− 1006(21)	5106(20)	2.8(3)
O(4)	—COO [−]	93(15)	1413(19)	3982(17)	2.1(3)
O(5)	—COO [−]	− 292(17)	− 246(21)	1501(19)	2.7(3)
O(6)	—COO [−]	1587(16)	653(20)	945(18)	2.4(3)
O(7)	H ₂ O	2092(23)	− 1938(24)	2837(26)	4.1(4)
O(8)	H ₂ O	2966(23)	1863(24)	5923(26)	4.1(4)
O(9)	H ₂ O	1688(20)	2945(23)	2837(23)	3.5(4)
O(10)	H ₂ O	5746(50)	3005(55)	2749(55)	4.6(1.0)
C(1)		4991(16)	474(25)	4433(19)	1.4(3)
C(2)		351(20)	− 709(26)	5310(24)	1.9(4)
C(3)		565(21)	− 254(28)	161(24)	2.0(4)

^a The anisotropic thermal parameters for neodymium, calculated from the expression: $\exp[-(h^2\beta_{11} + hk\beta_{12} + \dots)]$, are $\beta_{11} = 0.0035(1)$, $\beta_{22} = 0.0013(10)$, $\beta_{33} = 0.0051(1)$, $\beta_{12} = -0.0002(2)$, $\beta_{13} = 0.0045(1)$ and $\beta_{23} = 0.0002(2)$, resulting in root mean square displacements along the principal axis of the thermal ellipsoid, $R_1 = 0.078$ (Å), $R_2 = 0.132$ (Å), and $R_3 = 0.144$ (Å).

where x , y , z are the atomic coordinates given in Table 3. The composition of the three independent ligands referred to as ligand 1, ligand 2, and ligand 3 is shown in Fig. 1.

The structure of $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10.5\text{H}_2\text{O}$ is composed of infinite neodymium oxalate layers, perpendicular to the b -axis and situated around $y = 0$ and $y = 1/2$. The layers are held together by hydrogen bonds *via* water molecules situated between the layers. Fig. 1 shows part of the layer around $y = 0$ together with the water oxygen atoms above and below, projected along b .

Each ligand is coordinated to two metal atoms forming two chelates. Ligand 1 and ligand 2 link the metal atoms in chains running parallel with a and ligand 3 links these chains together to form a network (see Fig. 1).

Adjacent layers are related to each other by the c -glides. In this way fairly large "free spaces" are left around the symmetry centres $(1/2, 0, 0)$ and $(1/2, 1/2, 1/2)$. The located water molecules are situated in these vacancies leaving a cavity around the symmetry center in which the missing water molecules may be situated. This possibility will be further discussed below.

The coordination polyhedron. The neodymium atom is coordinated by nine oxygen atoms, contributed by three oxalate groups and three water molecules. The coordination polyhedron formed is shown in Fig. 2. The water oxygen atoms O(7), O(8), and O(9) and the three carboxylic oxygen atoms O(2), O(3), and O(5) of the ligands Nos. 1, 2, and 3 respectively, are situated at the corners of a distorted trigonal prism. The remaining three carboxylic oxygen atoms O(1), O(4), and O(6) are located outside the midpoints of the "rectan-

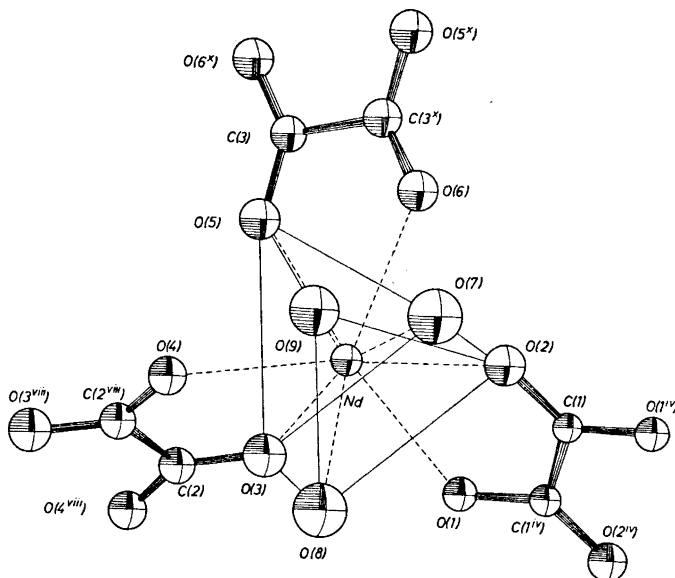


Fig. 2. The coordination around the neodymium atom with the trigonal prism outlined, drawn by the program ORTEP.⁴

gular" faces of the prism. This coordination geometry is not uncommon for oxygen coordinated lanthanoid ions. It is found, *e.g.*, in $\text{NH}_4\text{Y}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$,¹² $\text{Na}_3(\text{M}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3) \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$,¹³ and $\text{Gd}(\text{HOCH}_2\text{OCO})_3$.¹⁴

Selected interatomic distances within the coordination polyhedron are given in Table 4. Neither of the triangular faces of the prism O(2)–O(8)–O(9) and O(3)–O(5)–O(7) are equilateral but they are of about the same size, both having one side considerably longer than the other two. These long sides, O(2)–O(8) and O(3)–O(5), are not edges of the same "rectangular" face (see Fig. 2). The triangular faces are not parallel; the angle between the planes is 7°. The four distances O(1)–O(7), O(1)–O(8), O(2)–O(6), and O(4)–O(5) between oxygen atoms not belonging to the same ligand are in the interval 2.78–2.86 Å, *i.e.* about twice the van der Waals radius of oxygen,¹⁵ indicating contacts between these oxygen atoms.

The neodymium-oxygen bond distances are all close to 2.50 Å (Table 4). There is no significant difference between the carboxylic and the water oxygen atoms in this respect.

The ligands. The dimensions of the oxalate ions (see Table 5) agree with those found in other oxalate structures.¹⁶ The differences in length between the individual C–O bonds are not significant.

The three independent oxalate ions all have a center of symmetry and thus the two O–C–O planes cannot be twisted with respect to each other as found, *e.g.*, in $(\text{N}_4\text{H})_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$.¹⁷ The total bond angle around the carbon atom is 360(3)° in all three ligands, but since this angle is very insensitive

Table 5. Selected interatomic distances (Å) and angles (°), with estimated standard deviations, within the ligands.

A. Ligand 1.

Distance		Angle	
C(1)—C(1 ^{iv})	1.47(4)	O(1)—C(1)—O(2)	124(2)
C(1)—O(1)	1.27(2)	O(1)—C(1)—C(1 ^{iv})	117(2)
C(1)—O(2)	1.26(3)	O(2)—C(1)—C(1 ^{iv})	118(2)

B. Ligand 2.

Distance		Angle	
C(2)—C(2 ^{viii})	1.56(5)	O(3)—C(2)—O(4)	127(2)
C(2)—O(3)	1.22(3)	O(3)—C(2)—C(2 ^{viii})	118(2)
C(2)—O(4)	1.28(2)	O(4)—C(2)—C(2 ^{viii})	115(2)

C. Ligand 3.

Distance		Angle	
C(3)—C(3 ^x)	1.59(4)	O(5)—C(3)—O(6)	129(2)
C(3)—O(5)	1.25(3)	O(5)—C(3)—C(3 ^x)	116(2)
C(3)—O(6)	1.25(3)	O(6)—C(3)—C(3 ^x)	116(2)

to small separations between the two parallel O—C—O planes, the planarity of the ligands cannot be judged from this fact. A separation of this type has been found for the oxalate ion of $K_2C_2O_4 \cdot H_2O$.¹⁶ The deviations of the ligand atoms from the respective least squares planes through the ligands are given in Table 6. These deviations correspond to separations between the O—C—O planes in the ligands Nos. 1, 2, and 3, respectively, of 0.05, 0.05, and 0.07 Å, but are not significant. Thus the oxalate groups are planar within the limits of errors.

The water content. According to chemical analysis the structure should contain 21 water molecules per unit cell. Only 14 of these have been located in the X-ray investigation. The remaining seven water molecules are probably situated in the free spaces around the symmetry centres (1/2,0,0) and (1/2,1/2,1/2).

The space around (1/2,0,0) (see Fig. 1 and 3) is bounded by two parallel, approximately planar six-membered rings of water molecules situated around the levels $y = 1/4$ (O(7^v), O(10), O(8ⁱ), O(9ⁱ), O(8ⁱⁱⁱ), O(10ⁱ)) and $y = -1/4$ (O(9^{vi}), O(8^{iv}), O(10^{vi}), O(7ⁱⁱ), O(10^{vii}), O(8^{vi})) and by ligand 1ⁱ and ligand 1ⁱⁱ.

Table 6. The deviations in Å of the ligand atoms from the respective least squares planes through the ligands. The lower signs refer to the superscripted atoms.

Ligand 1		Ligand 2		Ligand 3	
Atom	Distance	Atom	Distance	Atom	Distance
C(1), C(1 ^{iv})	±0.01	C(2), C(2 ^{viii})	∓0.01	C(3), C(3 ^x)	∓0.01
O(1), O(1 ^{iv})	∓0.00	O(3), O(3 ^{viii})	±0.00	O(5), O(5 ^x)	±0.00
O(2), O(2 ^{iv})	∓0.00	O(4), O(4 ^{viii})	±0.00	O(6), O(6 ^x)	±0.00

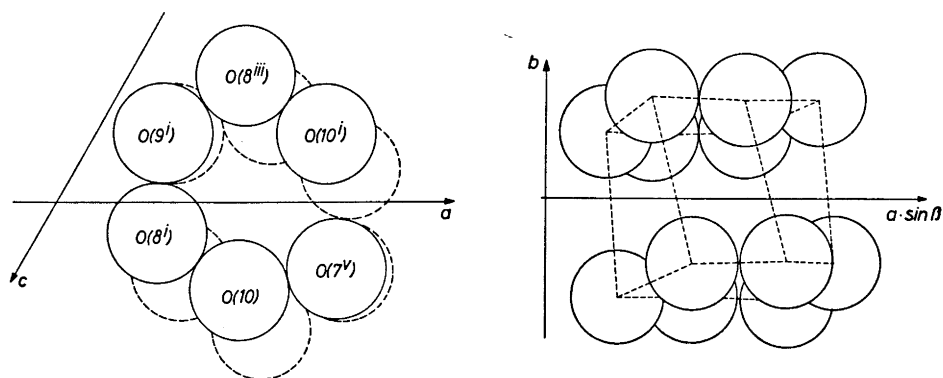


Fig. 3. The twelve water molecules bounding the cavity at $(1/2, 0, 0)$ projected along b and c . The water molecules are represented by spheres of radius 1.4 Å.

The distance between neighbouring oxygen atoms within a ring are 2.86–2.99 Å except for the distance O(7ⁱⁱ)–O(10^v) which is 4.12 Å. The shortest distance between two oxygen atoms in different rings is 4.92 Å. The corresponding distance in a hexagonal closest-packed arrangement of spheres with the radius 1.4 Å is 4.5 Å. In such an arrangement there are five spheres within the space bounded by two six-membered rings. The available space is even larger than indicated above since the position O(10) is only half occupied. It thus seems possible for at least five spheres of radius 1.4 Å to be included in the cavity. The actual maximum number of water molecules may be less than five since all geometrically possible arrangements are not consistent with the formation of a reasonable hydrogen bond system.

To account for the seven unlocated water molecules there would be on the average 3.5 water molecules per cavity. These may be arranged in several different ways, which is probably the reason why they are not detected in the Fourier maps. One favourable position of a water oxygen might be (0.40, 0.46, 0.38) where a high peak is found in the final difference synthesis (see p. 2972).

The varying water content obtained for the compounds $M_2(C_2O_4)_3 \cdot nH_2O$ of this crystal structure might be explained by an inclusion of different amounts

of water in the cavities, depending on the conditions of crystal growth. The powder diffraction patterns are identical for neodymium oxalates with $n = 10.0$ and $n = 10.6$ and for cerium oxalates with $n = 10.0$ and $n = 11.0$ indicating that the crystal structures are the same for different values of n .

The values of n do commonly fall in the range 10–11 in the beginning of the series of isomorphous lanthanoid oxalates and in the range 9–10 in the end of this series. The highest value reported is $n = 12$ for the Ce-compound,¹⁸ which, if the position O(10) is fully occupied as is found for $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ and $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$,² would correspond to four water molecules per cavity.

The decrease in water content through the isomorphous series is probably due to the fact that the dimensions of the cavity are decreasing with the decreasing crystal radius of the metal ion. This may result in a decrease of the most favourable number of water molecules per cavity.

Possible hydrogen bonds. The hydrogen atoms and 1/3 of the water oxygen atoms of the structure are not located and hence only some possibilities of hydrogen bonding can be discussed. On energetic grounds the hydrogen atoms of the coordinated water molecules are expected to point away from the neodymium ion and therefore hydrogen bonds between oxygen atoms belonging to the same coordination polyhedron are not probable.

Table 7. Possible hydrogen bond distances (Å) and some angles (°) involved with estimated standard deviations. Distances less than 3.20 Å between water oxygen atoms and oxygen atoms not belonging to the same coordination polyhedron are given.

Distance	Angle
O(7 ^v)—O(4 ^{xi}) 2.82(3)	O(4 ^{xi})—O(7 ^v)—O(10) 117(1)
O(7 ^v)—O(10) 2.87(6)	O(4 ^{xi})—O(7 ^v)—O(3 ^{iv}) 43(1)
O(7 ^v)—O(3 ^{iv}) 3.18(3)	O(3 ^{iv})—O(7 ^v)—O(10) 74(1)
O(8 ⁱ)—O(6) 2.90(3)	O(9)—O(8 ⁱ)—O(6) 59(1)
O(8 ⁱ)—O(10) 2.86(6)	O(9)—O(8 ⁱ)—O(2) 58(1)
O(8 ⁱ)—O(9) 3.00(3)	O(9)—O(8 ⁱ)—O(10) 110(1)
O(8 ⁱ)—O(2) 3.12(3)	O(6)—O(8 ⁱ)—O(2) 55(1)
O(9)—O(5 ^{ix}) 2.69(3)	O(6)—O(8 ⁱ)—O(10) 115(1)
O(10)—O(1 ^{iv}) 2.75(5)	O(2)—O(8 ⁱ)—O(10) 65(1)
	O(5 ^{ix})—O(9)—O(8 ⁱ) 133(1)
	O(8 ⁱ)—O(10)—O(1 ^{iv}) 103(2)
	O(8 ⁱ)—O(10)—O(7 ^v) 134(2)
	O(1 ^{iv})—O(10)—O(7 ^v) 107(2)

Distances suitable for hydrogen bond formation outside the coordination polyhedron are listed in Table 7 together with some bond angles of interest. It is seen that each of the located water molecules may form one hydrogen bond to a carboxylic oxygen atom *viz.* O(7^v)—O(4^{xi}), O(8ⁱ)—O(6), O(9)—O(5^{ix}), and O(10)—O(1^{iv}). The corresponding distances are 2.69–2.89 Å and the bond angles around the carboxylic oxygen atoms fall in the range 101–136°, which seems reasonable. The Nd—O—O angles involved are 104–123° and thus the hydrogen atoms are well separated from the

neodymium ions. The hydrogen bonds $O(7^v) - O(4^{xi})$, $O(8^i) - O(6)$, and $O(9) - O(5^{ix})$ are formed between oxygen atoms coordinated to neodymium atoms of adjacent layers (see Fig. 4).

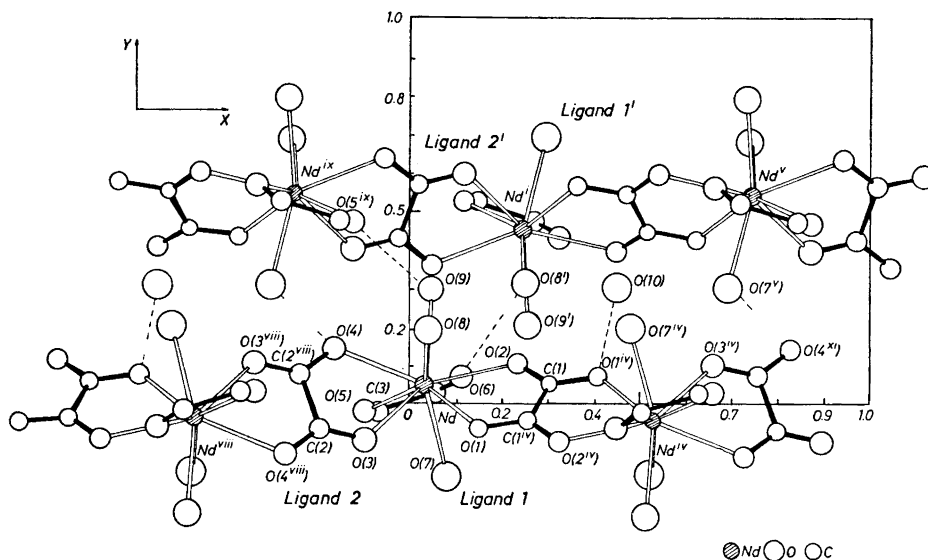


Fig. 4. Parts of two adjacent neodymium-oxalate chains projected onto (001) along $c \sin \beta$. The coordinated water oxygen atoms and half of the ligand 3 of each metal atom are included together with the water oxygen atoms $O(10)$ situated between the chains. Possible hydrogen bonds between water and carboxylic oxygen atoms are marked with dashes. The figure is drawn by the program ORTEP.⁴

There are no other carboxylic oxygen atoms within hydrogen bond distance from $O(9)$ and $O(10)$. $O(2)$ is situated 3.12 \AA from $O(8^i)$, and $O(3^{iv})$ 3.18 \AA from $O(7^v)$, but these cannot be hydrogen bonds formed by the second hydrogen atom of $O(8^i)$ and $O(7^v)$ because the angles $O(6) - O(8^i) - O(2)$ and $O(4^{xi}) - O(7^v) - O(3^{iv})$ are only 55° and 43° , respectively. The remaining hydrogen atoms of $O(7) - O(10)$ probably interact with neighbouring water molecules.

As described above the unlocated water molecules are assumed to be situated in cavities in the structure. These cavities are bounded by water molecules bonded to different neodymium oxalate layers; $O(7) - O(9)$ are coordinated to Nd and $O(10)$ hydrogen bonded to $O(1^{iv})$. The water molecules within the cavity are probably hydrogen bonded to the surrounding water oxygen atoms and to each other and may in this way form additional bonds between the layers.

The neodymium-oxalate layers are thus held together by hydrogen bonds formed between oxygen atoms belonging to different layers: (i) directly ($O(7^{ix}) - O(4)$, $O(8^i) - O(6)$, and $O(9) - O(5^{ix})$), and (ii) indirectly *via* the water molecules in the cavities.

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