Structural Studies on the Rare Earth Carboxylates

21. On the Positions of the Water Molecules in Hexa-aquo Tris-oxalato Dineodymium(III) 4½-Hydrate at −50°C

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One third of the water molecules of $Nd_2(C_2O_4)_3.10\frac{1}{2}H_2O$ are disordered at room temperature. The structure has been redetermined at −50°C and several new water positions with occupancies in the range $0.3 - 0.5$ have been found. They are located in cavities in the structure, and are within hydrogen bond distance $(2.7 - 3.2$ Å$)$ from each other and from the oxygens surrounding the cavity.

According to chemical analysis the compound $Nd_2(C_2O_4)_3.nH_2O$ (NDOX) should contain 10.5 mol of water per formula unit. NDOX is commonly described as a decahydrate but values of n larger than 10 have been reported by Wylie [1] and by the present author.[2] An X-ray structure analysis [2] showed that six of the water molecules were coordinated to neodymium. Only one of the uncoordinated water molecules could be located and it became necessary to assume that the remaining water molecules (3.5 per formula unit) were disordered in the cavities formed by the packing of the neodymium oxalate complexes. This situation often arises when large "empty" spaces are left between layers, molecules or complex ions in compounds which crystallize from water solution.[3] The main function of such disordered water molecules seems to be that of filling space and they should be only weakly attached to the surrounding atoms and to each other.

In some structures of this type,[4-6] maxima in the electron density, interpretable as water molecules with temperature factors in the range $10 - 25$ Å^2, are found in the appropriate regions. These high temperature factors cannot be attributed to the thermal movement of a single atom but may be simulated by a random distribution of the water molecules among a number of favourable positions around that obtained in the structure refinement. Even in cases where no significant electron density is found it must be assumed that the included water molecules are located to certain favourable regions of the actual space rather than being distributed completely at random.

This localized disorder may be statistical or dynamic. In the latter case it is possible that the water molecules may be fixed at the most favourable position of each region when their thermal mobility is reduced. Then it should be possible to detect these water positions in a low temperature study of the structure.

In an attempt to locate the missing water molecules the structure of NDOX has been reinvestigated at $-50°C$. Unfortunately the crystal structure may not be stable at low temperature as indicated by diffuse and sometimes split reflexions. Thus the accuracy in the determination is fairly low but since new water positions were actually found the result is given here.

EXPERIMENTAL

The preparation and analysis of the crystals have been described before.[2] A crystal of the dimensions $0.10 \times 0.10 \times 0.30$ mm³ mounted in a glass capillary along the 0.30 mm edge was used in recording the layers $hk0 - hk5$, with the Weissenberg, multi-film technique. Ni-filtered Cu-radiation was used and the temperature was $-50°C$. The low temperature equipment was of the type described by Olovsson.[7] The intensities of 756 independent reflexions were measured visually by comparison with a calibrated scale. Corrections for the Lorentz, polarisation and absorption effects were applied to the intensity data. The linear absorption coefficient was 371 cm⁻¹ and the transmission factors were in the range $0.05 - 0.17$.

The room-temperature unit cell parameters, $a = 11.68$ Å, $b = 9.65$ Å, $c = 10.28$ Å, and $\beta = 118.9°$ were used in the refinement. Judging from Weissenberg and oscillation photographs the changes in cell edges between room-temperature and $-50°C$ were less than 0.05 Å and that in β less than 0.5°. The space group is $P2_1/c$ (No. 14)[8] and $Z = 4$.

All computation work was carried out on the UNIVAC 1108 computer at Lund, Sweden, using the programs DRF, DATAP2, LALS, DISTAN, and LINUS.[9]

DETERMINATION OF THE WATER POSITIONS

The electron density maps of a $F_o - F_c$ synthesis based on the room-temperature positions of the neodymium ion, the oxalate ions, and the coordinated water oxygens, revealed five peaks of height $1 - 2$ e/Å³, at positions suitable for water oxygens. These positions are denoted W1, W2, W3, W4, and W5 in Table 1. Several of them are too close together to be simultaneously occupied (see Table 4A).

The positional parameters of all atoms including W1 – W5, isotropic temperature factors, and inter layer scale factors together with the occupancies, G, of W1 – W5 were refined by full-matrix least squares calculations. After six cycles the shifts in all parameters were less than 10 % of their estimated standard deviations and the valus of the varied occupancies were $G_{w1} = 0.65(14)$, $G_{w2} = 0.52(13)$, $G_{w3} = 0.39(11)$, $G_{w4} = 0.32(11)$, and $G_{w5} = 0.30(13)$. It is obvious that the standard deviations are too large to permit any accurate determination of the water content.

Among the conditions on the occupancies derivable from the "too close" distances given in Table 4 A, are $G_{w1} + G_{w2} \leq 1$ and $G_{w3} + G_{w4} + G_{w5} \leq 1$. In view of the large estimated standard deviations both conditions appear to be met but in a following refinement the occupancies $G_{w1} - G_{w5}$ were fixed at the values 0.5, 0.5, 0.4, 0.3, and 0.3, respectively. The agreement factor

Table 1. Atomic parameters with estimated standard deviations for the compound $Nd_2(C_2O_4)_3 \cdot 10\frac{1}{2}H_2O$ at $-50°C$. B denotes the isotropic temperature factor and G the occupancy of the position.

Atom	Group	G	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$B/Å^2$
Nd			1887(2)	468(2)	3569(3)	2.4(1)
O(1)	COO⁻		3934(23)	−704(20)	5548(34)	3.0(5)
O(2)	COO⁻		3914(23)	1014(24)	3522(35)	3.5(5)
O(3)	COO⁻		1265(24)	−989(23)	5065(36)	3.4(5)
O(4)	COO⁻		89(22)	1454(23)	4000(33)	3.4(4)
O(5)	COO⁻		−327(26)	−240(23)	1515(45)	3.5(5)
O(6)	COO⁻		1653(29)	698(28)	929(44)	4.4(6)
O(7)	H_2O		2101(24)	−1866(22)	2812(36)	3.6(5)
O(8)	H_2O		2991(28)	1903(27)	5885(41)	4.5(6)
O(9)	H_2O		1630(25)	2938(26)	2791(40)	4.2(5)
C(1)			5010(36)	450(33)	4484(54)	3.5(6)
C(2)			324(29)	−680(26)	5329(47)	2.4(6)
C(3)			559(35)	178(33)	−305(72)	3.4(7)
W1	H_2O	0.5	4244(57)	−1898(58)	2273(83)	4.9(1.3)
W2	H_2O	0.5	4343(86)	−2904(86)	3009(117)	8.2(2.1)
W3	H_2O	0.4	3368(69)	−972(69)	6(100)	4.6(1.5)
W4	H_2O	0.3	3818(84)	552(81)	−1063(131)	3.6(1.6)
W5	H_2O	0.3	4155(87)	82(87)	176(133)	3.6(1.6)

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$ converged to 0.122 and $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ to 0.155. The refinement procedure was the same as described in Ref. 2 and the weighting scheme used was $w = 1/(20 + |F_o| + 0.008|F_o|^2 + 0.0005|F_o|^3)$. The final atomic parameters are given in Table 1 and the observed structure factors are compared to those calculated in the last cycle in Table 2. The shifts in all parameters were less than 1 % of their estimated standard deviations in this cycle.

Judging from the conditions given above the sum of the occupancies used for W1−W5 is the maximum possible. It corresponds to a total water content of 10 mol per formula unit i.e. lower than that indicated by chemical analysis. A difference synthesis based on the parameters given in Table 1 revealed, besides a peak of about 5 e/Å³ at the position of neodymium, a number of peaks 1−2 e/Å³. Three of them had positions suitable for additional water oxygens viz. (0.59, −0.06, 0.18), (0.37, −0.03, −0.11), and (0.48, −0.00, 0.00), but it was not possible to refine oxygen at these positions. The structure may, however, contain disordered water even at low temperature and thus the hydration number 10.5 is not excluded by the present analysis.

The water position W1 was found already in the room-temperature study of NDOX.[2] The electron density maps of the final difference synthesis of that work showed a peak, 3e/Å³, approximately at the position W4 and also wide regions of positive electron density, about 1 e/Å³, around W2 and W3. The positions W2−W5 were tentatively included in a new refinement of the room-temperature structure. This refinement was successful for W2 and W3 but not for W4 and W5. The positional parameters arrived at for W1, W2, and

Table 2. Observed and calculated structure factors in $Nd_2(C_2O_4)_3 \cdot 10\frac{1}{2}H_2O$ at the temperature $-50°C$. In each group the running index h, $|F_o|$, and $|F_c|$ are given.

Table 3. Positional parameters of the disordered water molecules W1, W2, and W3 at room temperature. B denotes the isotropic temperature factor and G the occupancy of the position.

Atom	G	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$B/\text{Å}^2$
W1	0.5	5685(52)	3098(60)	2812(60)	4.3(1.0)
W2	0.5	5719(95)	2431(112)	2190(112)	9.0(2.3)
W3	0.4	6797(197)	4166(209)	4995(209)	14.9(5.1)

W3 at room temperature are given in Table 3. The R-value was reduced by 0.002 by the introduction of W2 and W3.

The structure of NDOX has also been determined by Ollendorff and Weigel.[10] They found the water positions W1 ($G = 0.5$, $B = 8.0$) and W5 ($G = 0.6$, $B = 5.0$). Thus the low temperature study confirms the water positions discernible from the two room temperature investigations.

DESCRIPTION OF THE WATER ARRANGEMENT

The room temperature structure of NDOX has been described in detail in Ref. 2, and only a brief recapitulation of the general features will be given here. Superscripts of the following significance are used to indicate equivalent sites in the structure.

x,y,z
(i) $1-x,\bar{y},\bar{z}$
(ii) $x,1/2-y,z-1/2$
(iii) $x,-y-1/2,z-1/2$
(iv) $1-x,y-1/2,1/2-z$

(v) $1-x,1/2+y,1/2-z$
(vi) $1-x,\bar{y},1-z$
(ix) $x,y,z-1$
(x) $x,-y-1/2,z-1/2$

(xi) $1-x,\bar{y},1-z$
(xx) $1+x,\bar{y},z$
(vv) $\bar{x},\bar{y},\bar{z}$

The structure is composed from neodymium oxalate layers parallel with the ac-plane and located around $y = 0$ and $y = 1/2$. The layer around $y = 0$ is shown in Fig. 1. The ligands Nos. 2 and 3 link the neodymium ions in zig zag chains running in the z-direction. These chains are in turn linked in layers by ligand 1. Three water molecules O(7), O(8), and O(9) are coordinated to neodymium and are situated above and below the layer at $y \approx 1/4$ and $y \approx -1/4$. Adjacent layers are related by the c-glide. They are held together by hydrogen bonds formed between the water molecules of one layer and the carboxylate oxygens in the zig zag chains of the next layer, *viz.* O(9ii) – O(5vv), O(8ii) – O(6), and O(7iii) – O(4vv).

With this way of packing of the layers fairly large "empty" spaces are left around the symmetry centers $(1/2,0,0)$ and $(1/2,1/2,1/2)$. The uncoordinated water molecules are located in these cavities. Including W1 the cavity around $(1/2,0,0)$ is surrounded by two water hexagons *viz.* W1i, O(8ix), O(9ii), O(8ii), W1v, and O7v at $y \approx 1/4$ and W1x, O(7iii), W1, O(8xi), O(9iv), O(8iv) at $y \approx -1/4$ and by ligand 1ii and ligand 1iv at $y \approx 1/2$ and $y \approx -1/2$, respectively. The water hexagons around adjacent cavities share the edge O(8) – W1, *e.g.*
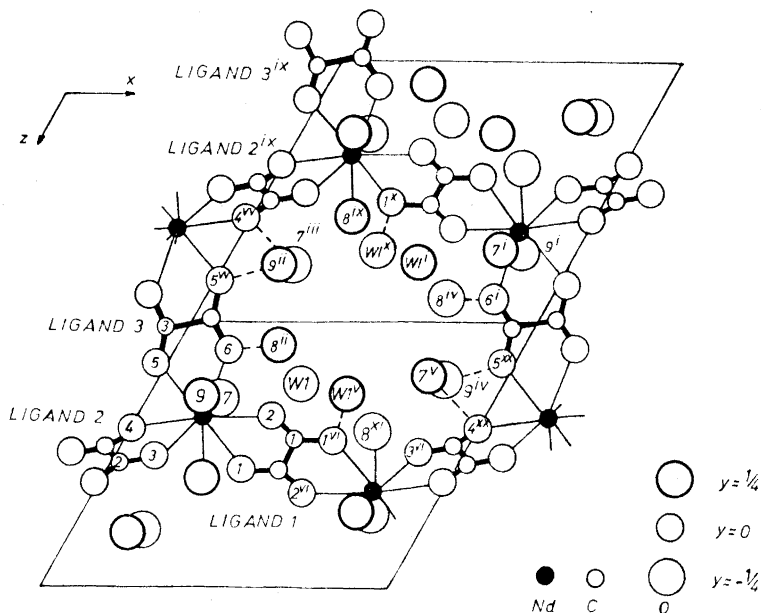
Fig. 1. The neodymium oxalate layer around $y = 0$ projected onto (0J0), with $-0.32 \leq y \leq 0.32$, *i.e.* the water oxygens above and below the layer are included. Bonds within the oxalate ions are filled, metal-oxygen bonds are single lines, and possible hydrogen bonds are marked with dashes.

$O(8^{ix}) - W1^i$ of the upper hexagon around (1/2,0,0) belongs to the lower hexagon around (1/2,1/2,1/2).

This part of the structure is not drastically changed by the decrease in temperature. Because of the low accuracy obtained in both determinations it is not possible to make any detailed comparison of bond distances and angles between the two temperatures. This feature is illustrated in Table 4 B which gives the possible hydrogen bond distances of the coordinated water molecules at room temperature and at $-50°C$.

Table 4 C gives for each of the water molecules $W1 - W5$ the distances to all neighbours within the range $2.60 - 3.20$ Å. These distances are regarded as representing possible hydrogen bonds.[11] W1 and W2 are hydrogen bonded to the coordinated water molecules O(7) and O(8) and to the carboxylate oxygen O(1); *cf.* $W1^x$ and $W2^x$ in Fig. 2 a and b, respectively. The distance $W1 - W2$ is 1.20 Å and thus either W1 or W2 is present. They may both be regarded as belonging to the hexagons surrounding the cavity. There are four pairs $W1 - W2$ around each cavity. Four water molecules may be distributed among these eight sites in ten non-equivalent ways. The possible arrangements around (1/2,0,0) are given in Table 5.

Within the cavity are six possible water sites, *viz.* W3, W4, W5, and their centrosymmetric equivalents $W3^i$, $W4^i$, and $W5^i$. These sites are close to

Table 4. Selected interatomic distances (Å) with estimated standard deviations in
$Nd_2(C_2O_4)_3.10\frac{1}{2}H_2O$.

A. Distances shorter than 2.60 Å between possible water positions at $-50°C$.

W1 – W2	1.20(11)	W4 – W5	1.22(17)
W1 – W3	2.23(11)	W4 – W5^i	2.17(12)
W3 – W4	2.05(12)	W5 – W5^i	2.18(19)
W3 – W5	1.32(11)		

B. Possible hydrogen bond distances of the water molecules coordinated to Nd(III),
at $-50°C$ and at room temperature.

	$-50°C$	Room temperature		$-50°C$	Room temperature
$O(7^v) - O(4^{xx})$	2.83(3)	2.83(3)	$O(8^{ii}) - O(2)$	3.12(4)	3.12(3)
$O(7^v) - W1^v$	2.81(7)	2.96(6)	$O(8^{ii}) - O(6)$	2.81(4)	2.90(3)
$O(7^v) - W2^v$	2.72(9)	2.62(10)	$O(8^{ii}) - O(9)$	3.07(5)	3.03(3)
$O(7^v) - W3^i$	2.90(8)	2.89(20)	$O(8^{ii}) - W1^v$	2.85(7)	2.82(6)
$O(9^{ii}) - O(5^{vv})$	2.64(4)	2.69(3)	$O(8^{ii}) - W2^v$	2.92(9)	2.91(10)
$O(9^{ii}) - O(8^{ix})$	3.07(5)	3.00(3)	$O(8^{ix}) - W4$	3.09(12)	—
$O(9^{ii}) - W4$	2.67(9)	—			

C. Possible hydrogen bond distances at $-50°C$ of the water molecules not coordinated
to Nd(III).

$W1^x - O(1^x)$	2.83(7)	$W3^i - W2^v$	2.99(13)
		$W3^i - W4$	2.95(11)
$W1^x - O(8^{iv})$	2.85(7)	$W3^i - W5$	3.11(12)
$W1 - W5$	2.84(13)		
		$W4 - O(8^{ix})$	3.09(12)
$W2^x - O(1^x)$	2.70(11)	$W4 - O(9^{ii})$	2.67(9)
$W2^x - O(7^{iii})$	2.72(9)	$W4 - W2^x$	2.90(12)
$W2^x - O(8^{iv})$	2.92(9)	$W4 - W3^i$	2.95(11)
$W2^x - W3$	2.99(13)	$W4 - W4^i$	2.78(19)
$W2^x - W4$	2.90(12)	$W4 - W2^v$	3.19(15)
$W2 - W4^i$	3.19(15)		
$W2^x - W5$	3.15(14)	$W5 - W1$	2.84(13)
$W2^v - W5$	2.68(13)	$W5 - W2^v$	2.68(13)
		$W5 - W2^x$	3.15(14)
$W3^i - O(6^i)$	3.06(8)	$W5 - W3^i$	3.11(12)
$W3^i - O(7^v)$	2.90(8)		

each other and at most two of them may be simultaneously occupied. Four
non-equivalent combinations are possible. They are denoted A, B, C, and D
in Table 5. The distance W1 – W3 is 2.24 Å which means that those combina-
tions of surrounding and included water molecules that contain the pair
W1 – W3 or W1^i – W3^i are not allowed. There remains 27 possible combina-
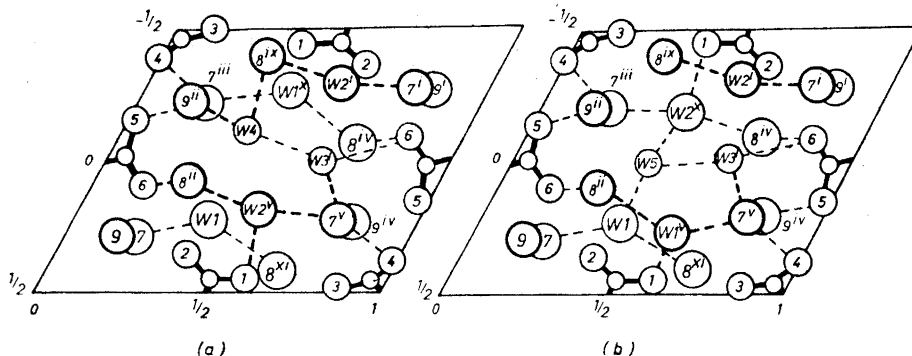tions and none of them seem to be more probable than the other.

Fig. 2. Possible arrangements of water molecules around (1/2,0,0). The y-range projected and the notation of the atoms and bonds are the same as in Fig. 1.

Table 5. Possible arrangements of the disordered water molecules around (1/2,0,0). The signs + and − denote possible and impossible combinations, respectively.

Water molecules in the hexagons	A: W4 − W4^i	B: W3^i − W5	C: W3^i − W4	D: W3 − W3^i
I. W1,W2^v,W2^i,W1^x	+	+	+	−
II. W2,W1^v,W2^i,W1^x	+	+	+	+
III. W1,W1^v,W2^i,W2^x	+	+	+	−
IV. W1,W2^v,W1^i,W2^x	+	−	−	−
V. W2,W2^v,W2^i,W1^x	+	+	+	+
VI. W1,W2^v,W2^i,W2^x	+	+	+	−
VII. W1,W1^v,W1^i,W2^x	+	−	−	−
VIII. W1,W1^v,W2^i,W1^x	+	+	+	−
IX. W1,W1^v,W1^i,W1^x	+	−	−	−
X. W2,W2^v,W2^i,W2^x	+	+	+	+

The bonding situation of the water pairs A, B, and C may in all possible surroundings be described in the following way. The two water molecules are weakly attached to each other, with oxygen-oxygen distances of 2.7 − 3.1 Å. The distances to the surrounding oxygens are in the range 2.9 − 3.2 Å except for W4 − O(9^{ii}) and W5 − W2^v which are both 2.7 Å. The probable hydrogen bonds in the arrangements IIC and IIIB are shown as examples in Fig. 2 a and b, respectively. Some cavities may contain W3 and W3^i. In these cases the two included water molecules are not hydrogen bonded to each other since the distance W3 − W3^i is 4.25 Å.

The function of W1 and W2 seems to be different from that of W3, W4, and W5. W1 and W2 are engaged in hydrogen bonded water chains terminating at neodymium ions of adjacent neodymium oxalate chains, *e.g.* Nd^{ix} − O(8^{ix}) − W2^i − O(7^i) − Nd^i and Nd^{iii} − O(7^{iii}) − W1^x − O(8^{iv}) − Nd^{iv} (see Fig. 2 a). Thus the role played by W1 and W2 is that of linking adjacent neodymium

oxalate chains in the x-direction. W3 and W4 may also take part in chains of this type, *e.g.* $Nd^{ii} - O(9^{ii}) - W4 - W4^i - O(9^{iv}) - Nd^{iv}$ and $Nd^{ii} - O(9^{ii}) - W4 - W3^i - O(7^v) - Nd^v$ (see Fig. 2 a). Since these chains are not always present they are probably not essential as links in the structure and the main function of W3 and W4 seems to be that of filling space. W5 may link adjacent water chains in the y-direction, $W1 - W5 - W2^v$, or in the z-direction, $W1 - W5 - W2^x$ (see Fig. 2 b), but also W5 must be regarded as mainly filling out space.

Thus, even though the exact arrangement of the disordered water molecules has not been determined it is obvious that the preferred positions are those where they may be hydrogen bonded to each other and to the surrounding oxygens. In this way the included water molecules are involved in the linking of the structure at the same time as they fill out the space between the main structural elements.

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