

Structural Studies on the Rare Earth Carboxylates

7. The Crystal and Molecular Structure of Tri-aquo-imino-diacetato-neodymium(III) Chloride

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The crystal and molecular structure of the lanthanoid-iminodiacetate compound $\text{Nd}(\text{OCOCH}_2\text{NHCH}_2\text{OCO})\text{Cl}\cdot 3\text{H}_2\text{O}$ has been determined and refined from three-dimensional X-ray intensity data. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ and with $Z=4$. The unit cell dimensions are $a=8.356\pm 0.001$ Å, $b=14.164\pm 0.002$ Å, and $c=8.424\pm 0.001$ Å. The structure has been refined to $R=0.087$. The iminodiacetate ions form bridges between the neodymium ions. The coordination polyhedron around the neodymium ion might be described as a distorted tricapped trigonal prism formed by eight oxygen atoms and one nitrogen atom. The Nd-O distances are in the range 2.39–2.78 Å. The nitrogen atom is situated in the equatorial plane of the prism at a distance of 2.67 Å from the neodymium ion. Four water oxygen atoms and one nitrogen atom are hydrogen bonded to the chloride ion, forming a distorted tetragonal pyramid. These polyhedra are connected by one water molecule thus forming chains in the a -direction.

One of the research programmes at this Institute is a series of X-ray crystal structure analyses of compounds between the trivalent rare earth ions and the related dicarboxylate ligands oxydiacetate,¹ iminodiacetate,² and thiodiacetate. In solution, these ligands form mononuclear complexes with the lanthanoids, and the formation constants for corresponding species increase in the order thiodiacetate³ < oxydiacetate⁴ < iminodiacetate.⁵⁻⁷ It is of interest to see if it is possible to correlate the behaviour in solution with properties such as coordination geometries, coordination numbers and steric effects, which can be established in the solid state by diffraction methods. One suitable series of iminodiacetate compounds to investigate is $\text{M}(\text{OCOCH}_2\text{NHCH}_2\text{OCO})\text{Cl}\cdot n\text{H}_2\text{O}$, $\text{M}=\text{Pr}-\text{Lu}$, $n=2, 3$ reported by Prutkova *et al.*⁸ An earlier attempt to prepare these compounds resulted in solids of the composition $\text{M}_2(\text{OCOCH}_2\text{NH}_2\text{CH}_2\text{OCO})_2\cdot(\text{OCOCH}_2\text{NHCH}_2\text{OCO})\text{Cl}_2\cdot 7\text{H}_2\text{O}$, $\text{M}=\text{Ce}-\text{Gd}$, the crystal and molecular structure of which have been described

in a preliminary report.² Closer examinations of the pH in the solution from which the crystals are obtained showed that it has to be greater than 4.5 for the formation of the series reported by Prutkova *et al.* In this paper, the crystal and molecular structure of tri-aquo-iminodiacetate neodymium(III) chloride, $\text{Nd}(\text{OCOCH}_2\text{NHCH}_2\text{OCO})\text{Cl}\cdot 3\text{H}_2\text{O}$ is described, and it is referred to as NIC below.

EXPERIMENTAL

Preparation and analysis. Equimolar water solutions of neodymium chloride and neodymium iminodiacetate were mixed and the pH of the solution was adjusted to 5. Slow evaporation at room temperature gave a microcrystalline precipitate. In order to get crystals large enough for single crystal work the sparingly soluble precipitate was treated with water at 80°C in a sealed glass tube for three weeks.

After drying at 60°C, the compound was analysed for Nd, H₂O, C, N, and H (the last three elements by Division of Analytical Chemistry, Lund). The relative amounts found are compared with those calculated for $[\text{Nd}(\text{C}_4\text{H}_7\text{NO}_4)(\text{H}_2\text{O})_3]\text{Cl}$, F.W. 364.8. (Found: Nd 39.3; C 12.9; N 3.7; H 3.6; H₂O 14.8. Calc.: Nd 39.5; C 13.2; N 3.8; H 3.0; H₂O 14.8.)

Single-crystal work. The method of preparation results in crystals which are tabular (010). The intensity data were recorded with the integrated Weissenberg multiple film technique. Ni-filtered Cu radiation was used. The intensities of 947 reflections of the layers $hk0-hk7$ were measured by a flying spot integrating microdensitometer (manufactured by Joyce, Loebel & Co. Ltd., Gateshead, England). The crystal used had a rather regular shape with the dimensions $0.09 \times 0.03 \times 0.06 \text{ mm}^3$. In a second setting, a single crystal with the dimensions $0.15 \times 0.04 \times 0.10 \text{ mm}^3$ was used to record the layers $h0l-h11l$. The intensities of 986 reflexions were measured visually by using a calibrated scale.

The intensity data were corrected for Lorentz, polarisation, and absorption effects. The linear absorption coefficient μ is 370 cm^{-1} . The transmission factor, evaluated by numerical integration, varied in the intervals 0.08–0.38, and 0.02–0.26 for the data from the first and the second setting, respectively.

UNIT CELL AND SPACE GROUP

NIC crystallizes in the orthorhombic system. The systematically absent reflexions are $h00$ with $h \neq 2n$, $0k0$ with $k \neq 2n$, and $00l$ with $l \neq 2n$. The only possible space group is thus $P2_12_12_1$ (No. 19).⁹

As mentioned above (p. 1206) it is possible to prepare isostructural compounds with the same composition as NIC for all lanthanoid ions except Ce(III). Their unit cell dimensions have been determined from powder photographs recorded in a Guinier–Hägg focusing camera with $\text{CuK}\alpha$ -radiation, as will be described in a following paper in this series.

The following crystal data were obtained for NIC:

$$\begin{array}{ll} a = 8.356 \pm 0.001 \text{ \AA} & D_m = 2.37 \text{ g/cm}^3 \\ b = 14.164 \pm 0.002 \text{ \AA} & D_x = 2.43 \text{ g/cm}^3 \\ c = 8.424 \pm 0.001 \text{ \AA} & Z = 4 \\ V = 997.0 \pm 0.2 \text{ \AA}^3 & \end{array}$$

The density D_m was determined by the displacement method.

DETERMINATION AND REFINEMENT OF STRUCTURE

The position of the neodymium ion was deduced from a three-dimensional Patterson synthesis. After three cycles of least-squares refinement of the preliminary atomic parameters of neodymium and the interlayer scale factors, a three-dimensional ($F_o - F_c$) synthesis based upon the neodymium position was calculated. The chloride ion was placed at the position of the highest peak in the electron density maps. The atoms of the ligand molecule were found by geometrical considerations. The three water molecules were placed at positions of peaks located at coordination distances from the neodymium ion.

The preliminary atomic coordinates, isotropic temperature factors, and inter-layer scale factors were improved with full-matrix least-squares refinement. The quantity minimized was

$$\sum w(|F_o| - |F_c|)^2$$

with weights w chosen according to Cruickshank.¹⁰ Only reflexions with $0.67 < |F_o|/|F_c| < 1.50$ were included in the refinement. After five cycles, the discrepancy factor

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

was 0.095 for the intensity material obtained in the b -setting. The material obtained in the c -setting gave $R=0.088$ after five cycles. All observed reflexions were included in the calculations of R . At this stage, the data were brought together. Seven more cycles resulted in $R=0.087$. After the last cycle of refinement, the shifts in the parameters were less than 0.01 % of the estimated standard deviations.

Further refinement using anisotropic thermal parameters was performed. Since the weighted discrepancy factor

$$wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

Table 1. Atomic parameters with estimated standard deviations. B denotes the isotropic temperature factor.

| Atom | Group | $x \times 10^4$ | $y \times 10^4$ | $z \times 10^4$ | $B/\text{Å}^2$ |
|------|--------------------|-----------------|-----------------|-----------------|----------------|
| Nd | | 3446 (1) | - 855 (1) | 6342 (1) | 1.15 (3) |
| Cl | | 13526 (11) | - 3290 (5) | 10578 (9) | 2.9 (1) |
| O(1) | -COO- | 3359 (21) | 2 (11) | 3720 (19) | 1.6 (2) |
| O(2) | -COO- | 4289 (22) | 152 (13) | 1245 (23) | 2.1 (3) |
| O(3) | -COO- | 7226 (23) | - 3156 (12) | 5613 (20) | 1.5 (3) |
| O(4) | -COO- | 5139 (23) | - 2286 (26) | 6271 (26) | 2.5 (3) |
| O(5) | H ₂ O | 1986 (27) | - 2011 (15) | 8006 (26) | 2.5 (4) |
| O(6) | H ₂ O | 5183 (29) | - 847 (18) | 8675 (31) | 3.9 (4) |
| O(7) | H ₂ O | 4101 (25) | 823 (15) | 6790 (24) | 2.6 (3) |
| C(1) | -COO- | 4421 (29) | - 107 (17) | 2711 (27) | 1.4 (4) |
| C(2) | -CH ₂ - | 5819 (31) | - 782 (20) | 3018 (30) | 2.1 (4) |
| C(3) | -CH ₂ - | 7369 (37) | - 1486 (21) | 5251 (37) | 2.7 (5) |
| C(4) | -COO- | 6583 (41) | - 2343 (21) | 5743 (34) | 3.0 (5) |
| N | -NH- | 6211 (26) | - 704 (16) | 4787 (26) | 2.0 (4) |

only changed from 0.0965 to 0.0964 in three cycles it was concluded that the structure could be described just as well with isotropic temperature factors assigned to all atoms.

Table 1 gives the final atomic parameters with their estimated standard deviations. A three-dimensional ($F_o - F_c$) synthesis based upon these parameters showed only small peaks above a slowly varying background except at the position (0.34, 0.91, 0.16) where a peak with the approximate height $2 e/\text{\AA}^3$ appeared. Since the distances from this peak to O(2) and O(7) are 1.65 Å and 2.11 Å, respectively, it was judged as spurious.

The atomic scattering factors used in the calculations were taken from *International Tables*¹¹ (Cl, O, N, and C) and from Cromer *et al.*¹² (Nd). The scattering factors were not corrected for anomalous dispersion, nor have the values of F_o been corrected for extinction effects. Observed and calculated structure factors of NIC are compared in Table 2.

The weighting scheme was analysed for constancy of the average values of $w(|F_o| - |F_c|)^2$ between different intervals of the $|F_o|$ and $\sin \theta$ values. The analyses obtained in the last cycle of the refinement are given in Table 3, and it is seen that the weighting scheme used is reasonable.

Table 3. Analyses of the weighting scheme $w = 1/(30 + |F_c| + 0.012|F_o|^2)$ obtained in the last cycle of refinement. The averages $\overline{w(|F_o| - |F_c|)^2} = w\Delta^2$ are normalized.

| $ F_o $ interval | $\overline{w\Delta^2}$ | Number of reflexions | $\sin \theta$ interval | $\overline{w\Delta^2}$ | Number of reflexions |
|---------------------|------------------------|-------------------------|---------------------------|------------------------|-------------------------|
| 0-26 | 0.84 | 95 | 0.00-0.42 | 1.36 | 105 |
| 26-32 | 1.13 | 112 | 0.42-0.53 | 0.92 | 96 |
| 32-37 | 1.17 | 111 | 0.53-0.60 | 1.00 | 98 |
| 37-41 | 1.24 | 114 | 0.60-0.66 | 1.18 | 83 |
| 41-46 | 0.97 | 113 | 0.66-0.71 | 0.88 | 87 |
| 46-52 | 0.88 | 113 | 0.71-0.76 | 0.86 | 87 |
| 52-60 | 1.02 | 114 | 0.76-0.80 | 1.01 | 84 |
| 60-73 | 1.06 | 113 | 0.80-0.84 | 0.81 | 76 |
| 73-92 | 0.78 | 114 | 0.84-0.87 | 0.90 | 82 |
| 92-189 | 0.89 | 115 | 0.87-0.90 | 1.08 | 75 |

Selected interatomic distances and angles in the structure are given in Table 4. The standard deviations were calculated from the estimated standard deviations of the atomic coordinates and the unit cell dimensions.

All computations were made on the CDC 3600 computer in Uppsala, Sweden, and the programmes used were CELSIUS, DRF, LALS, DISTAN, PLANE, ORTEP, and DATAP2.¹³

DESCRIPTION OF THE STRUCTURE

The structure of NIC contains one independent ligand. Its atoms are designated in Fig. 1. The superscripts (*i*) - (*ix*) are used to indicate the following equivalent sites in the structure

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

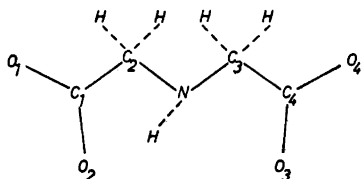


Fig. 1. Designation of the atoms in the iminodiacetate ion.

where x, y, z are the atomic coordinates given in Table 1. The structure is built up of a three-dimensional network of cross-linked neodymium-ligand chains, as is seen in Fig. 2. Ligand 1 is coordinated to Nd, Nd^{iv}, and Nd^v.

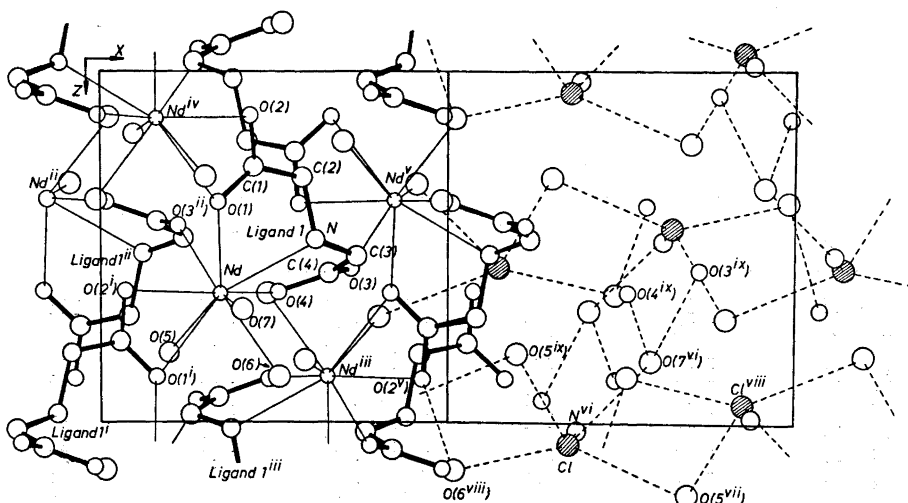


Fig. 2. A projection on (010) of two unit cells of NIC. The left part of the figure shows the cross-linked neodymium-ligand chains, and the right part shows possible hydrogen bonds. The figure is drawn by the program ORTEP.¹³

The coordination polyhedron. The neodymium atom is coordinated by eight oxygen atoms and one nitrogen atom. The coordination polyhedron, a distorted tricapped trigonal prism, is shown in Fig. 3. The three carboxylate oxygen atoms O(1), O(2ⁱ), O(4), and the three water oxygen atoms O(5), O(6), and O(7) are situated at the corners of the trigonal prism. The carboxylate oxygen atoms O(3ⁱⁱ), O(1ⁱ) and the nitrogen atom N are located in the equatorial plane of the prism outside the midpoints of the "rectangular" faces. The same type of coordination polyhedron is found for many lanthanoid complexes, e.g. in Gd(HOCH₂OCO)₃,¹⁴ Nd₂(C₂O₄)₃·10.5H₂O,¹⁵ Na₃[Yb(OCOC₅H₃NOCO)]·14H₂O,¹⁶ and Na₃[M(OCOCH₂OCH₂OCO)₃]·2NaClO₄·6H₂O.¹ Contrary to the planar

ligands in the tris(oxydiacetato)⁻¹ and tris(dipicolinato)complexes,¹⁶ reported earlier in this series, the ligand is bent and not located in a diagonal plane of the trigonal prism, but has its coordinated carboxylate oxygens, O(1) and O(4), on the same edge of the prism with the nitrogen atom outside a midpoint of a "rectangular" face (*cf.* Fig. 3). Bond distances in the coordination polyhedron are given in Table 4 A. The coordination polyhedra are connected by sharing the carboxylate oxygen atom O(1) (Fig. 2), thus forming chains in the *c*-direction, and the Nd–Nd distances within the chains are 5.12 Å. The neodymium-iminonitrogen distance 2.67 Å is rather long compared with the ytterbium-nitrogen distances (2.33 Å and 2.41 Å) found in orthorhombic ytterbium dipicolinate.¹⁶ The angles Nd–N–C(2) and Nd–N–C(3) are 107° and 112°, respectively, indicating that the free electron pair of the nitrogen atom might point towards the neodymium ion. In spite of the long Nd–N distance, a coordination link between these two atoms is thus not excluded, as is also reported by Prutkova *et al.*⁸ Of the 21 contact distances within the coordination polyhedron, seven are in the range 2.84–2.99 Å, indicating van der Waals contacts.¹⁷

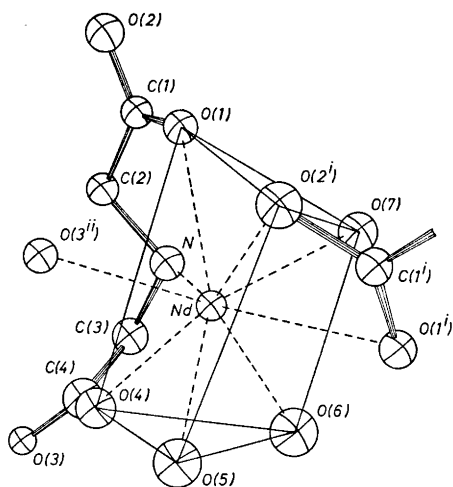


Fig. 3. The coordination around the neodymium ion with the trigonal prism outlined. The figure is drawn by the program ORTEP.¹³

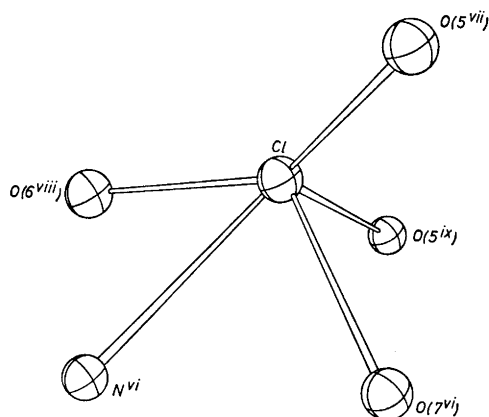


Fig. 4. The possible hydrogen bonds with the chloride ion. The figure is drawn by the program ORTEP.¹³

The ligand. The iminodiacetate ion acts as a tridentate ligand and forms two five-membered rings with the neodymium ion. The bond distances and bond angles are given in Table 4 B. The nitrogen-carbon distances, 1.52 Å and 1.53 Å, and the C–N–C angle, 110°, are within the range found in organic compounds containing iminogroups, *e.g.* diethylamine (C₂H₅)NH¹⁸ and trimethylamine boron trifluoride (CH₃)₃NBF₃.¹⁹ The C–C and C–O distances are compatible with those found in other structures of this type.^{2,14–16}

Table 4. Selected interatomic distances (Å) and angles (°) with estimated standard deviations.

A. The coordination polyhedron

| Distance | | Distance | |
|--------------------------|----------|---------------------------------------|----------|
| Nd—O(1) | 2.52 (2) | O(1 ⁱ)—O(6) | 3.19 (3) |
| Nd—O(1 ⁱ) | 2.78 (2) | O(1 ⁱ)—O(7) | 2.87 (3) |
| Nd—O(2 ⁱ) | 2.50 (2) | O(2 ⁱ)—O(3 ⁱ) | 3.13 (3) |
| Nd—O(3 ⁱⁱ) | 2.39 (2) | O(2 ⁱ)—O(5) | 3.21 (3) |
| Nd—O(4) | 2.48 (2) | O(2 ⁱ)—O(7) | 3.19 (3) |
| Nd—O(5) | 2.48 (2) | O(3 ⁱⁱ)—O(4) | 2.97 (3) |
| Nd—O(6) | 2.44 (3) | O(3 ⁱⁱ)—O(5) | 3.07 (3) |
| Nd—O(7) | 2.47 (2) | O(3 ⁱⁱ)—N | 3.72 (3) |
| Nd—N | 2.67 (2) | O(4)—O(5) | 3.04 (3) |
| O(1)—O(2 ⁱ) | 3.08 (3) | O(4)—O(6) | 2.87 (3) |
| O(1)—O(3 ⁱⁱ) | 2.84 (2) | O(4)—N | 2.72 (3) |
| O(1)—O(4) | 4.16 (3) | O(5)—O(6) | 3.19 (3) |
| O(1)—O(7) | 2.90 (3) | O(6)—O(7) | 2.99 (3) |
| O(1)—N | 2.74 (3) | O(6)—N | 3.39 (3) |
| O(1 ⁱ)—O(5) | 2.92 (3) | O(7)—N | 3.26 (3) |

B. The ligand

| Distance | | Angle | |
|-----------|----------|----------------|---------|
| C(1)—O(1) | 1.24 (3) | O(1)—C(1)—O(2) | 124 (2) |
| C(1)—O(2) | 1.29 (3) | O(1)—C(1)—C(2) | 121 (2) |
| C(4)—O(3) | 1.28 (4) | O(2)—C(1)—C(2) | 114 (2) |
| C(4)—O(4) | 1.29 (4) | O(3)—C(4)—O(4) | 119 (3) |
| C(1)—C(2) | 1.53 (4) | C(3)—C(4)—O(3) | 123 (3) |
| C(3)—C(4) | 1.44 (4) | C(3)—C(4)—O(4) | 118 (3) |
| N—C(2) | 1.53 (2) | C(1)—C(2)—N | 106 (2) |
| N—C(3) | 1.52 (4) | C(2)—N—C(3) | 110 (2) |
| | | N—C(3)—C(4) | 113 (3) |

C. Possible hydrogen bonds

| Distance | | Angle | |
|--|----------|---|---------|
| O(5 ^{vii})—Cl | 3.16 (2) | Cl—O(5 ^{vii})—Cl ^{viii} | 101 (1) |
| O(5 ^{vii})—Cl ^{viii} | 3.10 (2) | Cl—O(6 ^{viii})—O(2 ^v) | 107 (1) |
| O(6 ^{viii})—Cl | 3.11 (3) | Cl—O(7 ^{vi})—O(3 ^{ix}) | 123 (1) |
| O(6 ^{viii})—O(2 ^v) | 2.69 (3) | Cl—O(7 ^{vi})—O(4 ^{ix}) | 82 (1) |
| O(7 ^{vi})—Cl | 3.08 (2) | Cl—N ^{vi} —C(2 ^{vi}) | 90 (1) |
| O(7 ^{vi})—O(3 ^{ix}) | 2.85 (3) | Cl—N ^{vi} —C(3 ^{vi}) | 94 (1) |
| O(7 ^{vi})—O(4 ^{ix}) | 3.20 (3) | | |
| N ^{vi} —Cl | 3.44 (3) | | |

The least-squares planes through the C—COO groups have been calculated. As is seen in Table 5, their atoms are coplanar within 0.08 Å and 0.02 Å, respectively.

Table 5. The deviations (in Å) of the atoms from the least squares planes through the carboxylic groups.

| Atom | Distance | Atom | Distance |
|------|----------|------|----------|
| C(1) | -0.08 | C(3) | 0.01 |
| C(2) | 0.02 | C(4) | -0.02 |
| O(1) | 0.03 | O(3) | 0.01 |
| O(2) | 0.03 | O(4) | 0.01 |

Possible hydrogen bonds. On energetic grounds, the hydrogen atoms of the coordinated water molecules are expected to point away from the neodymium ion, and therefore hydrogen bonds within the coordination polyhedron are not probable. Distances less than 3.20 Å between water molecules and oxygen atoms and between water molecules and chloride ions are assumed as possible for hydrogen bond formation.²⁰ The shortest distance between the nitrogen atom and a chloride ion, 3.44 Å, is also compatible with a hydrogen bond,²¹ and this is supported by the angles Cl-N^{vi}-C(2^{vi}) and Cl-N^{vi}-C(3^{vi}), which are 90° and 94°, respectively. Possible hydrogen bonds are summarized in Table 4 C. The chloride ion seems to be hydrogen bonded to four water oxygen atoms and one nitrogen atom, and the polyhedron formed might be described as a distorted tetragonal pyramid (*cf.* Fig. 4). The polyhedra are connected by the water molecule O(5) thus forming chains in the *a*-direction (*cf.* Fig. 2), and the Cl-Cl distances within the chains are 4.84 Å. As O(1) is coordinated to two neodymium ions, a hydrogen bond between this carboxylate oxygen and a water molecule seems to be excluded, but the other three carboxylate oxygens might form one hydrogen bond each.

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