1176 *Inorg. Chem.* **1997,** *36,* 1176−1180

# Crystal Structure and Absorption Spectroscopy of a Neodymium(III) Complex with Triethylenetetraaminehexaacetic Acid, $Na_3[Nd(TTHA)]\cdot 2.5NaClO_4\cdot 7.617H_2O$

**Anna Mondry* and Przemysław Starynowicz**

Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

*Received May 7, 1996*⊗

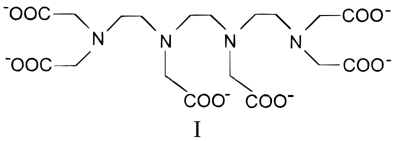
The crystal structure and absorption spectroscopy results of the $Na_3[Nd(TTHA)]\cdot 2.5NaClO_4\cdot 7.617H_2O$ compound are presented. The crystal structure of the complex was determined by X-ray analysis. Crystals are monoclinic, space group $C2/c$, with $a = 38.446(8)$ Å, $b = 10.552(2)$ Å, $c = 25.796(5)$ Å, $\beta = 130.51(3)°$, and $Z = 4$. The structure consists of monomeric (triethylenetetraaminehexaacetato)neodymate anions, perchlorate anions, sodium cations, and water molecules. The Nd(III) ion adopts a 10-coordinate geometry with six oxygen atoms and four nitrogen atoms from a ligand molecule, which is best described as a bicapped square antiprism. Absorption spectra of a single crystal were measured at room and liquid helium temperatures. Intensities of the f−f transitions were analyzed on the basis of Judd−Ofelt theory. The good correspondence between the spectra of $[Nd(TTHA)]^{3-}$ in solution and in the single crystal suggests close similarity of both coordination polyhedra.

## Introduction

The ability of polyamino polycarboxylic acids to form generally stable and readily soluble complexes over the entire pH range with a variety of metal ions is the reason for their extensive and diversified application. In this development ethylenediaminetetraacetic acid (EDTA) played a central role and stimulated interest in the higher homologues, such an diethylenetriaminepentaacetic (DTPA) or triethylenetetraaminehexaacetic acid (TTHA), in order to develop ligands with an increased affinity and selectivity for metal ions.

Some of these complexes have been utilized as contrast-enhancing agents in biomedical magnetic resonance imaging (MRI).[1] Among them the *N*-methylglucamine salt of the gadolinium−DTPA complex, $(NMG)_2[Gd(DTPA)]$, has been used clinically for this purpose for several years.[2] This is the reason why lanthanide complexes with this ligand and its variously substituted derivatives have recently become the subject of extensive investigations in solution[3−6] and in the solid state.[6−10]

Even though the Gd(III) complex with TTHA ligand (see structure **I**) has an acceptable toxicity profile, it is not probably suitable as a contrast agent. The first coordination sphere of this compound contains no labile water molecules, so its relaxivity in NMR spectroscopy is approximately half that of $(NMG)_2[Gd(DTPA)]$.[1]



I

However, stability, thermodynamic and structural properties of lanthanide complexes with TTHA have been widely studied,[11−19] since the ligand has been proposed for a variety of analytical uses.

To date, no solid state X-ray structure determination of a complex of this ligand with any lanthanide ion is known.[20] Two structure determinations have been reported for the Cr(III)[21] and vanadyl[22] complexes. In both cases TTHA has been shown to act as a decadentate ligand forming dinuclear complexes. However, none of these structures is relevant for modeling the structure of $[Ln(TTHA)]^{3-}$ complexes in solution. For a long time the opinion prevailed that the TTHA ligand cannot employ its full potential decadenticity in $[Ln(TTHA)]^{3-}$ complexes in solution and that one or more carboxylates remain uncoordinated to the metal ion.[11,12]

Studies that were performed recently on $[Ln(TTHA)]^{3-}$ complexes in solution indicate several different modes of TTHA coordination with light and heavy lanthanide ions; however, in both these cases there is no inner sphere water molecule. While the $^1H$ and $^{13}C$ NMR spectra of $[La(TTHA)]^{3-}$ complex indicate that each carboxylate and amine group of TTHA interacts directly with La(III) ion, the fluctional processes observed in the $^1H$ and $^{13}C$ NMR of the Y(III) and Lu(III) adducts are likely due to a ligand unwrapping/wrapping dynamics.[15] These data

---

* To whom correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1997.

(1) Lauffer, R. B. *Chem. Rev.* **1987,** *87,* 901.
(2) Niendorf, H. P. *Contrast Media in MRI*; Presented at the International Workshop, Bossum; Medicom: Berlin, 1990.
(3) Jenkins, B. G.; Laufer, R. B. *Inorg. Chem.* **1988**, *27,* 4730.
(4) Aime, S.; Botta, M. *Inorg. Chim. Acta* **1990,** *177,* 101.
(5) Watson, A. D. *J. Alloys Compd.* **1994,** *207/208,* 14.
(6) Franklin, S. J.; Raymond, K. N. *Inorg.Chem.* **1994,** *33,* 5794.
(7) Stezowski, J. J.; Hoard, J. L. *Isr. J. Chem.* **1984,** *24,* 323.
(8) Gries, H.; Miklautz, H. *Physiol. Chem. Phys. Med. NMR* **1984**, *16,* 105.
(9) Ehnebom, E.; Pedersen, B. F. *Acta Chem. Scand.* **1992,** *46,* 126.
(10) Inoue, M. B.; Inoue, M.; Fernando, Q. *Inorg. Chim. Acta* **1995,** *232,* 203.
(11) Yingst, A.; Martell, A. E. *J. Am. Chem. Soc.* **1969,** *91,* 6927.
(12) Gayhart, R. B.; Moeller, T. *J. Inorg. Nucl. Chem.* **1977,** *39,* 49.
(13) Choppin, G. R.; Baisden, P. A.; Khan, S. A. *Inorg. Chem.* **1979,** *18,* 1330.
(14) Wenzel, T. J.; Ashley, M. E.; Sievers, R. E. *Anal. Chem.* **1982,** *54,* 615.
(15) Holz, R. C.; Horrocks, W. DeW., Jr. *Inorg. Chim. Acta* **1990,** *171,* 193.
(16) Brittain, H. G. *J. Coord. Chem.* **1990,** *21,* 295.
(17) Chang, C. A.; Brittain, H. G.; Telser, J.; Tweedle, M. F. *Inorg. Chem.* **1990,** *29,* 4468.
(18) Mondry, A.; Riehl, J. P. *Acta Phys. Pol. A* **1993,** *84,* 969.
(19) Mondry, A.; Meskers, S. C. J.; Riehl, J. P. *J. Lumin.* **1994,** *62,* 17.
(20) After this work was submitted for publication, crystal structures of La(III) and Dy(III)−guanidinium−ttha complexes were reported: Ruloff, R.; Prokop, P.; Sieler, J.; Hoyer, E.; Beyer, L. *Z. Naturforsch.* **1996**, *51b*, 963.
(21) Fallon, G. D.; Gatehouse, B. M. *Acta Crystallogr.* **1974,** *B30,* 1987.
(22) Fallon, G. D.; Gatehouse, B. M. *Acta Crystallogr.* **1976,** *B32,* 71.

suggest that as the metal ion size decreases, the steric bulk of the TTHA ligand interposes causing incomplete metal−ligand binding. This allows either multiple 1:1 species to exist in which the ligand is involved in an unwrapping/wrapping processes or the coexistence of 2:1 and 1:1 metal:ligand species in solution. The results from the site-selective excitation spectroscopy and excited-state lifetime measurements[15] as well as from absorption spectroscopy[18] for $[Eu(TTHA)]^{3-}$ complex suggest the presence of two distinct 1:1 species which have identical unquenched lifetimes.

The studies on NMR-relaxivity measurements and the results from the fluorescence water counting[17] and energy transfer[16] indicate that Gd(III) and Tb(III) ions are fully coordinated by the TTHA ligand above pH 8 to form monomeric species, whereas below this pH value oligomeric species exist in solution.

Also CPL (circularly polarized luminescence) studies of Eu(III) and Tb(III) complexes with TTHA show that only the $[Eu(TTHA)]^{3-}$ complex is chiral and significantly stable to racemization.[19]

In this paper we report the solid-state X-ray structure and absorption spectroscopy of the $[Nd(TTHA)]^{3-}$ trisodium salt. Additionally, we report absorption results for some transitions of the $[Nd(TTHA)]^{3-}$ complex in solution to make a comparison between the structures of Nd(III) coordination polyhedron in aqueous solution and crystalline state.

## Experimental Section

**Materials and Sample Preparation.** A stock solution of neodymium perchlorate was prepared from $Nd_2O_3$ (99.9% Merck). The Nd(III) ion concentration was determined complexometrically using Xylenol Orange as an indicator. The stock solution of TTHA (98% Aldrich) was prepared by half-neutralization with NaOH. Single crystals of $[Nd(TTHA)]^{3-}$ complex were grown from aqueous-methanolic solution. Equimolar quantities of neodymium perchlorate and $Na_3H_3TTHA$ were mixed together to get 25 mL of starting solution with an Nd(III) concentration of 0.15 M. Next, the solid $NaClO_4$ was added to the solution in the molar proportion $NaClO_4$:Nd(III) = 10:1. The final pH was 4.50. The solution was slowly evaporated to dryness by heating at 40 °C and then dissolved in 20 mL of the 1:1 mixture of water to methanol (solution I). A beaker with the aqueous−methanolic $[Nd(TTHA)]^{3-}$ solution was covered by Parafilm and after a year a few single, pink-violet, parallelepiped crystals were grown, which were very resistant to air and humidity.

The Nd(III) ion concentration in the single crystals was determined complexometrically (1.6707 M). The refractive index $n$ of the crystal was assumed to be 1.50 and that of the solution medium to be 1.33.

Anal. Calcd (found) for $Na_3[Nd(C_{18}H_{24}O_{12}N_4]\cdot 2.5NaClO_4\cdot 7.6H_2O$: C, 18.88 (18.92); H, 3.43 (3.90); N, 4.89 (4.72).

An aqueous $[Nd(TTHA)]^{3-}$ solution (hereinafter solution II) was also prepared for a comparison of the spectral properties between an aqueous−methanolic solution with high concentration of Nd(III) ion, and an aqueous solution with low concentration of the metal.

The concentration of Nd(III) in the solution II was $2.219 \times 10^{-2}$ M, with a ligand-to-metal ratio 1.2:1, and the final pH = 7.65.

**X-ray Analysis.** A suitable crystal was cut from a larger one, and mounted on a Kuma KM4 diffractometer with $\kappa$ geometry and a graphite monochromator. The unit cell parameters were determined from angular settings of 25 reflections with $2\theta$ between 19 and 25°. The stability of data collection was monitored with three control reflections remeasured every 100 intensities. The data were corrected for Lorentz and polarization factors, but not for absorption or extinction. The position of the neodymium ion was found from a Patterson map; other atoms were found from subsequent difference Fourier syntheses. The C-bonded hydrogen atoms were placed from geometry, whereas the O-bonded ones were located on a difference Fourier map, not all of them found. The structure was refined with the full-matrix least-squares method with all ordered non-hydrogen atoms anisotropic and with disordered and hydrogen atoms isotropic. The (isotropic) temperature factors of Na5, Na51 and OW8, OW81 were constrained in pairs. Also the geometry of the Cl3 perchlorate ion was constrained to form the tetrahedron. The occupancy factors of Na5, Na51 and separately OW8, OW81, OW82 were refined, at the same time being constrained to sum up to 1 in each case. The calculations were performed with SHELXS[23] and SHELXL-93[24] programs. Other details of data collection and the structure refinement are given in Table 1.

**Table 1.** Crystallographic Data for $Na_3[Nd(TTHA)]\cdot 2.5NaClO_4\cdot 7.617H_2O$

empirical formula: $C_{18}H_{39.234}Cl_{2.5}N_4Na_{5.5}NdO_{29.617}$
fw = 1144.9
temperature: 293(2) K
wavelength: 0.710 73 Å
space group (No.): *C*2/*c* (15)
unit cell dimens:
  $a = 38.446(8)$ Å
  $b = 10.552(2)$ Å
  $c = 25.796(5)$ Å
  $\beta = 130.51(3)°$
$V = 7956(3)$ Å$^3$
$Z = 4$
$d_{measd} = 1.90$ Mg/m$^3$, by flotation in $CH_3Cl/CH_3Br$
$d_{calcd} = 1.911(1)$ Mg/m$^3$
abs coeff $\mu_{calc} = 1.66$ mm$^{-1}$
final $R$ indices $[I > 3\sigma(I)]$: $R(F) = 0.0352$, $R_w(F^2) = 0.0752^a$
no. of independent reflcns: 6521 $[R_{int} = 0.0311]$
refinement method: full-matrix least-squares on $F^2$
weights used: $w = 1/\sigma^2(F^2)$
data/restraints/params: 6521/22/604
goodness-of-fit on $F^2$: 3.267
largest diff peak and hole: +1.135 and −0.977 e Å$^{-3}$

[a] $R(F) = \sum|F_o - F_c|/\sum|F_c|$; $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

**Spectroscopic Measurements.** All absorption measurements of solutions and a single crystal were performed on a Cary 5 UV−vis−near−IR spectrophotometer in the region 300−920 nm. The crystal of good optical quality was checked by X-ray diffraction and recorded perpendicularly to the c axis using a spectrophotometer equipped with helium flow cryostat at 293 and 4 K.

The intensities of the 4f−4f transition ($P$) and values of the $\Omega_\lambda$ parameters were calculated from the following Judd−Ofelt[25,26] relation:

$$P = \chi \frac{8\pi^2 mc\sigma}{3h(2J+1)} \sum_{\lambda=2,4,6} \Omega_\lambda (f^n\psi J||U^{(\lambda)}||f^n\psi' J')^2 \qquad (1)$$

$P$ denotes the oscillator strength, $\chi = (n^2 + 2)^2/9n$, $n$ is the refractive index, $J$ is the total quantum number of the ground state, $(f^n\psi J||U^{(\lambda)}||f^n\psi' J')$ is the reduced matrix element of the unit tensor operator $U^{(\lambda)}$ tabulated by Carnall *et al.*,[27] and $\Omega_\lambda$ are empirical least-squares-fitted parameters.

## Results and Discussion

**Crystal Structure.** The geometry of the first coordination sphere of the Nd ion is presented in Table 2. The structure consists of the complex and perchlorate anions, sodium cations, and water of hydration. The complex is monomeric with 10-coordinate Nd cation wrapped up with triethylenetetraamine-hexaacetate ligand. The environment of the metal consists of four nitrogen and six carboxylate oxygen atoms located at typical distances from the metal and forming a distorted bicapped square antiprism, with N1 and N4 being the caps, and O8, O10, O12, N3 and O2, O4, O6, N2 forming the respective bases. An ORTEP[28] view of the complex anion is presented in Figure 1. The structure is held together by a network of hydrogen bonds

---

(23) Sheldrick, G. M. *Acta Crystallogr.* **1990,** *A46,* 467.
(24) Sheldrick, G. M. SHELXL-93—Program for Crystal Structure Refinement, University of Göttingen, 1993.
(25) Judd, B. R. *Phys. Rev.* **1962,** *127,* 750.
(26) Ofelt, G. S. *J. Chem. Phys.* **1962,** *37,* 511.
(27) Carnall, W. T.; Fields, P. R.; Rajnak, K. *J. Phys. Chem.* **1968,** *49,* 4424.

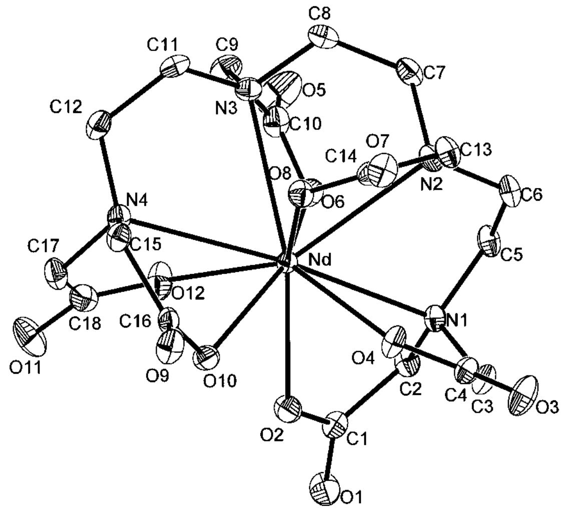


**Figure 1.** ORTEP view of the complex anion, together with the atom numbering scheme. The thermal ellipsoids are drawn at 30% probability. The sodium cations, perchlorate ions and solvating water were omitted for the sake of clarity.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg)

| | | | |
|---|---|---|---|
| Nd−O8 | 2.430(3) | Nd−O2 | 2.537(3) |
| Nd−O6 | 2.434(4) | Nd−N3 | 2.724(4) |
| Nd−O4 | 2.491(4) | Nd−N1 | 2.742(4) |
| Nd−O10 | 2.521(3) | Nd−N2 | 2.763(4) |
| Nd−O12 | 2.524(4) | Nd−N4 | 2.823(4) |
| O8−Nd−O6 | 126.7(2) | O6−Nd−N3 | 63.8(2) |
| O8−Nd−O4 | 69.3(2) | O4−Nd−N3 | 130.9(2) |
| O6−Nd−O4 | 129.1(2) | O10−Nd−N3 | 119.5(2) |
| O8−Nd−O10 | 73.7(2) | O12−Nd−N3 | 84.8(2) |
| O6−Nd−O10 | 153.3(2) | O2−Nd−N3 | 147.9(2) |
| O4−Nd−O10 | 71.1(2) | O8−Nd−N1 | 118.1(2) |
| O8−Nd−O12 | 132.1(2) | O6−Nd−N1 | 67.9(2) |
| O6−Nd−O12 | 67.0(2) | O4−Nd−N1 | 63.3(2) |
| O4−Nd−O12 | 143.7(2) | O10−Nd−N1 | 121.3(2) |
| O10−Nd−O12 | 86.6(2) | O12−Nd−N1 | 109.5(2) |
| O8−Nd−O2 | 142.2(2) | O2−Nd−N1 | 60.6(2) |
| O6−Nd−O2 | 89.3(2) | N3−Nd−N1 | 118.0(2) |
| O4−Nd−O2 | 79.3(2) | O8−Nd−N2 | 63.7(2) |
| O10−Nd−O2 | 76.7(2) | O6−Nd−N2 | 76.2(2) |
| O12−Nd−O2 | 67.7(2) | O4−Nd−N2 | 71.1(2) |
| O8−Nd−N3 | 69.2(2) | O10−Nd−N2 | 130.4(2) |
| O12−Nd−N2 | 141.2(2) | O10−Nd−N4 | 59.2(2) |
| O2−Nd−N2 | 125.1(2) | O12−Nd−N4 | 59.9(2) |
| N3−Nd−N2 | 67.8(2) | O2−Nd−N4 | 111.0(2) |
| N1−Nd−N2 | 64.8(2) | N3−Nd−N4 | 64.9(2) |
| O8−Nd−N4 | 72.6(2) | N1−Nd−N4 | 169.3(2) |
| O6−Nd−N4 | 106.9(2) | N2−Nd−N4 | 124.0(2) |
| O4−Nd−N4 | 123.6(2) | | |

and electrostatic interactions. Some of the sodium and perchlorate ions, as well as the water molecules, are disordered.

**Absorption Results.** The most sensitive transition for the changes of the lanthanide ion direct environment is the so called "hypersensitive" transition. It is interesting how this transition is reflected for the $[\mathrm{Nd(TTHA)}]^{3-}$ complex in solution and a single crystal. Such a comparison was made for the "hypersensitive" ${}^4I_{9/2} \rightarrow {}^4G_{5/2},{}^2G_{7/2}$ and the ${}^4I_{9/2} \rightarrow {}^4F_{3/2}$ transitions of Nd(III) ion and are presented in Figure 2.

Solution spectra shown in Figure 2 were recorded for the starting solution I and solution II. Also those for solution I after crystallization (not shown here) were taken. There were no essential differences between the oscillator strength values and the shapes of absorption bands of those three solutions.

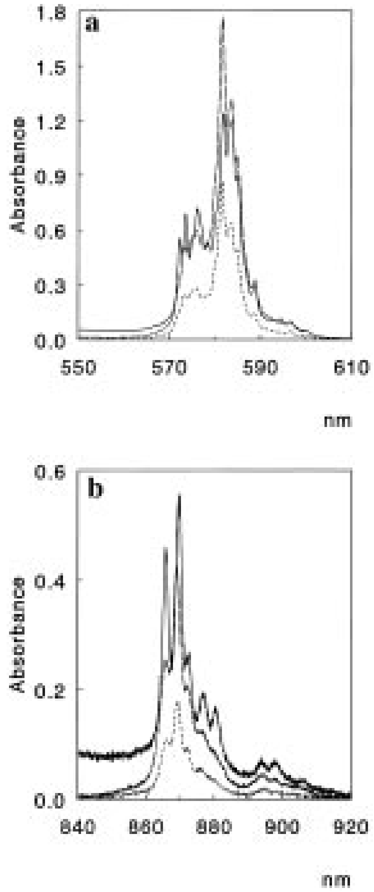


**Figure 2.** Absorption spectra for the $[\mathrm{Nd(TTHA)}]^{3-}$ complex in aqueous solution (- - -), in aqueous−methanolic solution (− −) and of the single crystal (—) at 293 K: (a) of the ${}^4I_{9/2} \rightarrow {}^4G_{5/2},{}^2G_{7/2}$ "hypersensitive" transition; (b) of the ${}^4I_{9/2} \rightarrow {}^4F_{3/2}$ transition. (For the aqueous solution $c_{\mathrm{Nd(III)}} = 2.219 \times 10^{-2}$ M, pH = 7.65, and $d = 2$ cm, for the aqueous−methanolic solution $c_{\mathrm{Nd(III)}} = 1.87 \times 10^{-1}$ M, pH = 4.5, and $d = 0.5$ cm, and for the single crystal $c_{\mathrm{Nd(III)}} = 1.6707$ M, and $d = 0.046$ cm).

Apart from that a high similarity between spectra of the $[\mathrm{Nd(TTHA)}]^{3-}$ complex in the liquid and solid phases is seen. However, a comparison between absorption spectra of the $[\mathrm{Nd(TTHA)}]^{3-}$ complex in solution and the single crystal reveals different crystal field splitting, which is seen for the ${}^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition (Figure 3). The splitting of the ${}^4I_{9/2}$ term given for the solution II (Figure 3a) exceeds the number of optical lines expected for the Nd(III) ion from the group theory. This confirms previous results for $[\mathrm{Eu(TTHA)}]^{3-}$ that above pH 6.00 two different 1:1 species of the same excited state lifetime exist in equilibrium.[15]

Our absorption spectroscopy results for the $\mathrm{Na_3[Nd(TTHA)]\cdot 2.5NaClO_4\cdot 7.617H_2O}$ crystal are consistent with the X-ray structure. The appearance of a single sharp peak of the ${}^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition for the crystal at 4 K (Figure 4a), as well as a splitting of the ${}^4F_{3/2}$ term into two optical lines, 11503 and 11568 cm$^{-1}$, is indicative of a single Nd(III) site.

The number of Stark components for the remaining transitions for the crystal at 4 K is not accordant with that expected for a single Nd(III) ion placed in a position with the $C_1$ site symmetry. The three most intensive absorption bands in the visible region of the $[\mathrm{Nd(TTHA)}]^{3-}$ crystal at 4 K are shown in Figures 4b and 5. It is clearly seen that there are more optical lines what could be expected from the relevant multiplicities $J + {}^1/_2$. Moreover, we can observe some components which are grouped in doublets. This increase of the number of the lines may be brought about either by the cooperative ion-pair effect, or by

---

(28) Johnson, C. K.; ORTEPII, *Report ORNL-5138;* Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

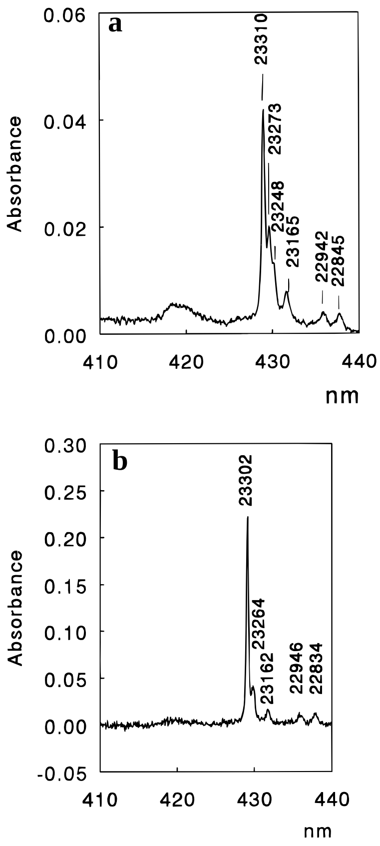


**Figure 3.** $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition for the $[Nd(TTHA)]^{3-}$ complex: (a) in the aqueous solution ($c_{Nd(III)} = 2.219 \times 10^{-2}$ M, pH = 7.65, $d = 2$ cm); (b) of the single crystal at 293 K ($c_{Nd(III)} = 1.6707$ M, $d = 0.0145$ cm).

the electron–phonon coupling.[29] The first effect may be neglected, because of long Nd(III)–Nd(III) distances in the crystal (the shortest are 9.515(8) Å). The electron–phonon coupling can be effected through a resonance of particular Stark components with vibrational modes associated with the lattice and/or internal ligand modes. The outer sphere disorder can also contribute to the additional splitting of electronic lines.

Detailed results of spectral intensities of the $Na_3[Nd(TTHA)]\cdot 2.5NaClO_4\cdot 7.617H_2O$ single-crystal spectra are presented in Table 3.

Our earlier studies on holmium[30,31] and neodymium[32] complexes showed that if in a solution a thermodynamically stable species with a structure similar to that in the solid state is present, then the intensities of the "hypersensitive" transition should be similar. This conclusion seems to be true also in our case.

The oscillator strength value of the $^4I_{9/2} \rightarrow {}^4G_{5/2},{}^2G_{7/2}$ Nd(III) ion transition is $1935.43 \times 10^{-8}$ for solution II. Our previous results on Nd(III)[32,33] complexes also indicated the importance of checking the $^4I_{9/2} \rightarrow {}^4F_{7/2},{}^4S_{3/2}$ and $^4I_{9/2} \rightarrow {}^4F_{5/2},{}^4H_{9/2}$ transition intensities in a solution and in a single crystal, respectively. If there is a significant difference between them, then at least one of the species existing in the solution should display a different symmetry as compared to that in the crystal.

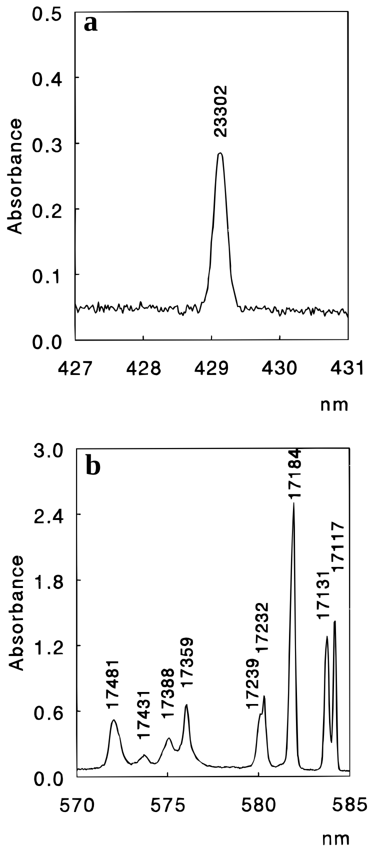


**Figure 4.** Absorption spectra for the $[Nd(TTHA)]^{3-}$ single crystal at 4 K of the following transitions: (a) $^4I_{9/2} \rightarrow {}^2P_{1/2}$; (b) $^4I_{9/2} \rightarrow {}^4G_{5/2},{}^2G_{7/2}$ ($c_{Nd(III)} = 1.6707$ M, $d = 0.0145$ cm).

**Table 3.** Oscillator Strength Values ($P_{exp}$, $P_{calc}$) and $\Omega_\lambda$ parameters for the $Na_3[Nd(TTHA)]\cdot 2.5NaClO_4\cdot 7.617H_2O$ Single Crystal at 293 and 4 K

| | $T = 293$ K | | $T = 4$ K |
|---|---|---|---|
| transition(s) $^4I_{9/2}\rightarrow$ | $10^8P_{exp}$ | $10^8P_{calc}$ | $10^8P_{exp}$ |
| $^4F_{3/2}$ | 328.84 | 288.43 | 223.95 |
| $^4F_{5/2}$, $^4H_{9/2}$ | 946.19 | 913.29 | 639.98 |
| $^4F_{7/2},{}^4S_{3/2}$ | 863.75 | 937.54 | 531.36 |
| $^4F_{9/2}$ | 70.40 | 73.55 | 36.59 |
| $^2H_{11/2}$ | 22.57 | 20.26 | 14.59 |
| $^4G_{5/2},{}^2G_{7/2}$ | 2076.51 | 2089.36 | 1319.92 |
| $^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$ | 856.77 | 686.82 | 624.30 |
| $^2K_{15/2}$, $^2G_{9/2}$, $(^2D,{}^2F)_{3/2}$, $^4G_{11/2}$ | 283.91 | 158.91 | 267.34 |
| $^2P_{1/2}$ | 61.73 | 73.18 | 47.28 |
| $^2D_{5/2}$ | 11.52 | 5.38 | |
| $^4D_{3/2}$, $^4D_{5/2}$, $^2I_{11/2}$, $^4D_{1/2}$ | 1359.62 | 1416.95 | 1005.08 |
| $10^{20}\Omega_2$ [cm$^2$] | $4.57 \pm 0.42$ | | |
| $10^{20}\Omega_4$ [cm$^2$] | $5.82 \pm 0.39$ | | |
| $10^{20}\Omega_6$ [cm$^2$] | $6.84 \pm 0.54$ | | |
| rms × $10^7$ | 8.39 | | |

The oscillator strengths for $[Nd(TTHA)]^{3-}$ in solution are $1030.57 \times 10^{-8}$ and $936.76 \times 10^{-8}$ for the $^4I_{9/2} \rightarrow {}^4F_{7/2},{}^4S_{3/2}$ and $^4I_{9/2} \rightarrow {}^4F_{5/2},{}^4H_{9/2}$ transitions, respectively.

Such a good correlation between the relevant values for the solution and the single crystal can testify that the symmetries of the species in solution are similar. This confirms also the results given by Holz and Horrocks[15] for $[Eu(TTHA)]^{3-}$ based on lifetime measurements and site selective-excitation spectroscopy. Even for a solution for which the observation of a single emission lifetime led to the conclusion that only 1:1 species was present, two peaks were observed for the $^7F_0 \rightarrow {}^5D_0$ transition.

As can be seen from Table 3, a decrease in intensity of almost all transitions in the single crystal with decreasing temperature

---

(29) Caro, P., Moune, O. K., Antic-Fidancev, E., Lemaitre-Blaise, M. *J. Less-Common Met.* **1985,** *112,* 135.

(30) Mondry, A. *Inorg. Chim. Acta* **1989,** *162,* 131.

(31) Mondry, A.; Bukietyńska, K. *Inorg. Chim. Acta* **1991,** *186,* 135.

(32) Mondry, A.; Starynowicz, P. *J. Alloys Compd.* **1995,** *225,* 367.

(33) Bukietyńska, K.; Mondry, A.; Pham Ngoc, T.; Starynowicz, P. *J. Alloys Compd.* **1995,** *225,* 52.

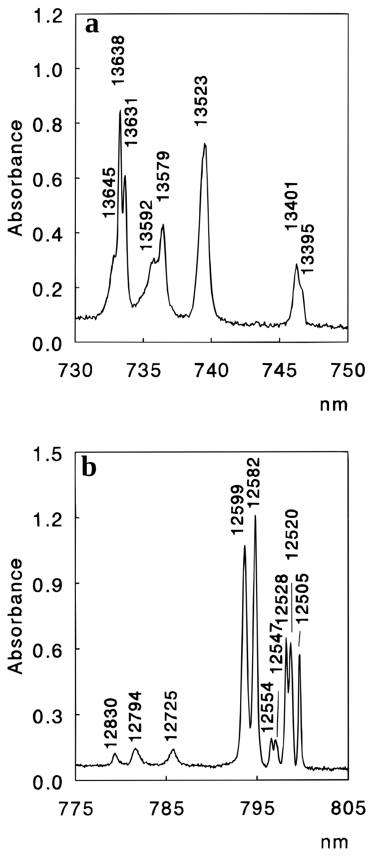


**Figure 5.** Absorption spectra for the $[Nd(TTHA)]^{3-}$ single crystal at 4 K for the following transitions: (a) $^4I_{9/2} \rightarrow {}^4F_{7/2}, {}^4S_{3/2}$; (b) $^4I_{9/2} \rightarrow {}^4F_{5/2}, {}^4H_{9/2}$ ($c_{Nd(III)} = 1.6707$ M, $d = 0.0145$ cm).

from 293 to 4 K is observed. It can be attributed to a change in the ground state population and/or by the vibronic mechanism.

Table 3 also lists the Judd–Ofelt $\Omega_\lambda$ parameter values. It is commonly believed that, of the three $\Omega_\lambda$ parameters, $\Omega_2$ is the most sensitive to the influence of the metal ion environment. Therefore it seems reasonable to compare it with data for other single crystals of Nd(III) ion compounds investigated so far. Thus, the $\Omega_2$ value for the $Na_3[Nd(TTHA)]\cdot 2.5NaClO_4\cdot 7.617H_2O$ is distinctly higher than that for the $K_3[Nd(NTA)_2\cdot H_2O]\cdot 5H_2O$[34] but very similar to that for the $(enH_2)[Nd_2(\alpha\text{-pic})_8]\cdot 6H_2O$ single crystal[34] (where $enH_2$ = ethylenediammonium and α-pic = α-picolinate = 2-pyridinecarboxylate).

The direct environment of Nd(III) ion in the case of the $[Nd(NTA)_2]^{3-}$ single crystal is composed of one water molecule, six carboxylic oxygen atoms, and two nitrogen atoms, whereas in $[Nd_2(\alpha\text{-pic})_8]^{2-}$ the coordination sphere consists of five carboxyl oxygen atoms and four nitrogen atoms. Although coordination numbers of these compounds are different, which implies a shorter metal–ligand distance as well as a lower energy of the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition for $[Nd_2(\alpha\text{-pic})_8]^{2-}$ (23 266 $cm^{-1}$),[34] it seems that the overall electron-donor abilities of those two different ligands are similar, and this is probably a reason for the good correspondence between $\Omega_2$ parameter values and oscillator strength values of the "hypersensitive" transition in these compounds. The much higher value $\Omega_6$ for $[Nd_2(\alpha\text{-pic})_8]^{2-}$ ($(10.50 \pm 0.66) \times 10^{20}$ $cm^2$)[34] than for $[Nd(TTHA)]^{3-}$ is probably brought about by the difference among the symmetries of the complexes and among the overall covalency effects.

## Conclusions

We succeded in getting a crystal of Nd(III) ion with the next after DTPA linear homologue of EDTA—triethylenetetraaminehexaacetic acid (TTHA). The crystal structure of the $Na_3[Nd(TTHA)]\cdot 2.5NaClO_4\cdot 7.617H_2O$ has been determined using X-ray diffraction.

The full coordination potential of the ligand was utilized in the mononuclear compound giving rise to the Nd(III) ion coordination number of 10. The coordination polyhedron of Nd(III) ion may be described as a bicapped square antiprism and consists of six carboxylate oxygen atoms and four amine nitrogen atoms with an average Nd–O distance of 2.49(5) Å and an Nd–N distance equal to 2.76(4) Å. This structure confirms the model of a structure of light lanthanide ion–TTHA species in solution, assumed by Holz and Horrocks.[15]

Our results from electronic absorption spectroscopy confirm the fact that the main species in solution has a coordination polyhedron very similar to the one found in the crystal.

Presently we are investigating another, dimeric complex of Nd(III) with TTHA with different spectroscopic properties.[35]

**Acknowledgment.** The authors would like to thank Prof. K. Bukietyńska for valuable discussions. This work was supported by Komitet Badań Naukowych (Committee of Scientific Research), grant 3 T09A 02010.

**Supporting Information Available:** Tables of crystallographic data, measurement details, atomic positional parameters, anisotropic thermal parameters, hydrogen coordinates, and interatomic distances and angles (15 pages). Ordering information is given on any current masthead page.

IC9604728

---

[34] Starynowicz, P.; Bukietyńska, K. *Polyhedron* **1994,** *13,* 109.

[35] Mondry, A.; Starynowicz, P. Manuscript in preparation.