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Crystal structure and absorption spectroscopy of a dimeric neodymium(III) complex with triethylenetetraaminehexaacetic acid (H_6ttha), $Na_{0.5}H_{5.5}[Nd_2(ttha)_2]\cdot 7.5NaClO_4\cdot 16.83H_2O$

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The crystal structure and absorption spectra (IR, UV/VIS) have been determined for $Na_{0.5}H_{5.5}[Nd_2(ttha)_2]\cdot 7.5NaClO_4\cdot 16.83H_2O$ (H_6ttha = triethylenetetraaminehexaacetic acid). The structure consists of the complex dimer, perchlorate anions, sodium cations and water of hydration. Both neodymium(III) ions are nine-co-ordinate. Each ttha ligand is bonded to one Nd^{III} through four of its carboxyl oxygen atoms and three of its nitrogen atoms. Two carboxyl oxygen atoms are bonded to the other Nd^{III}, and the fourth nitrogen atom remains unco-ordinated. The co-ordination spheres of both Nd^{III} are essentially the same and may be defined as distorted tricapped trigonal prisms. Absorption spectra of a single crystal were measured at room and liquid-helium temperatures. The intensities of the f–f transitions were analysed on the basis of Judd–Ofelt theory. Comparison of the absorption spectra of $[Nd(ttha)]^{3-}$ in solution to those of single crystals of $Na_3[Nd(ttha)]\cdot 2.5NaClO_4\cdot 7.617H_2O$ and $Na_{0.5}H_{5.5}[Nd_2(ttha)_2]\cdot 7.5NaClO_4\cdot 16.83H_2O$ compounds allowed us to estimate the ratio of mono- to di-meric species in solution.

Lanthanide ions form particularly stable complexes with polyamino polycarboxylic acids. This is the reason for their extensive and various applications.[1–5] Especially the studies of higher homologues of ethylenedinitrilotetraacetic acid (H_4edta), such as (carboxymethyl)iminobis(ethylenenitrilo)tetraacetic acid (H_5dtpa) and *N*,*N*′-bis(carboxymethyl)ethylenediiminobis(ethylenenitrilo)tetraacetic acid (triethylenetetraaminehexaacetic acid, H_6ttha), have given remarkable results. In order to recognize the potential use of these complexes, it is important to understand as much as possible the structure of and dynamic equilibria between species which exist in solution. These complexes generally have co-ordination numbers of eight to ten with flexible polyhedra. Although many techniques have been used for the determination of the shape of the co-ordination polyhedra, only X-ray diffraction can give a definite picture. However, this technique is generally limited to crystalline complexes, and it may be hazardous to speak of a certain co-ordination geometry in solution, nevertheless the structural information from X-ray crystallography can be very helpful to explain some properties of the complex in solution.

Extensive studies in solution and in the solid state have been made for complexes of Ln^{III} with dtpa[6–12] and its derivatives[13–24] because of its special applications. The complexes formed between Gd^{III} and dtpa or its bis(methylamide), are already approved contrast agents in NMR imaging.[25,26] So far, studies on lanthanide complexes with ttha have been carried out in solution[10,27–34] and for a long time no crystal structures of lanthanoid(III) complexes with this ligand were reported. Very recently, almost at the same time, a few crystallographic studies of such complexes have been published.[34–37] Two were reported for the guanidinium salts of complexes of La^{III} and Dy^{III} with ttha,[35] three for the potassium salts of La^{III}, Yb^{III}[36] and Gd^{III}[37] and one for the sodium salt of $[Nd(ttha)]^{3-}$.[34] The co-ordination number 10 is realized in the compounds of La^{III} and Nd^{III}, while those of Dy^{III} and Yb^{III} exhibit a co-ordination number of nine. All these complexes are monomeric and all four nitrogen atoms of the ligand are co-ordinated, while differences exist in the co-ordination of the carboxylic groups. The complex of Gd^{III} is binuclear:[37] each Gd^{III} is co-ordinated by three nitrogen atoms and four carboxyl oxygen atoms from one ttha and two carboxyl oxygen atoms from another ttha.

As far as the structure of the species in solution is concerned, our previous results[34] suggest that the main form existing in solution has a co-ordination polyhedron very similar to that found in the $Na_3[Nd(ttha)]\cdot 2.5NaClO_4\cdot 7.617H_2O$ crystal. We also succeeded in obtaining other crystals from the same solution from which the monomeric compound had been obtained. The new compound displayed different absorption properties from those of $Na_3[Nd(ttha)]\cdot 2.5NaClO_4\cdot 7.617H_2O$[34] and the X-ray study revealed its dimeric nature. The aim of this paper is to report the crystal structure of this neodymium(III) dimeric complex with ttha and the spectroscopic properties of its monocrystals.

Experimental

Materials and sample preparation

Crystals of $Na_{0.5}H_{5.5}[Nd(ttha)_2]\cdot 7.5NaClO_4\cdot 16.83H_2O$ were grown over about 2 y. A stock solution of neodymium perchlorate was prepared from Nd_2O_3 (99.9% Merck). The neodymium(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. Equimolar quantities of neodymium perchlorate and Na_3H_3ttha were mixed to give a starting solution (25 cm^3) with a neodymium(III) concentration of 0.15 M. Next, 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 dissolved in water–methanol (1 : 1, 20 cm^3). The beaker containing the solution was covered by Parafilm and after a year a few single crystals of a monomer, described elsewhere,[34] had grown and were removed. The remaining solution was left for another year and then the crystals of $Na_{0.5}H_{5.5}[Nd_2(ttha)_2]\cdot 7.5NaClO_4\cdot 16.83H_2O$ were obtained. The crystals are efflorescent contrary to the monomeric crystals reported earlier. The neodymium(III) ion concentration in the single crystal was determined by inductively coupled plasma–atomic emission spectroscopy (1.631 M). The refractive index *n* was assumed to be 1.50 [Found

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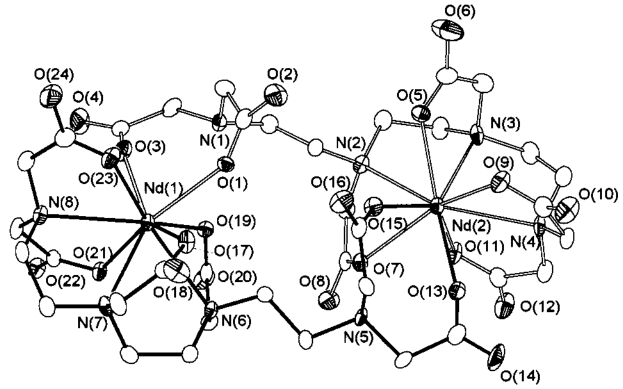

Fig. 1 An ORTEP[44] view of the complex anion, together with the atom numbering scheme. The thermal ellipsoids are drawn at 30% probability. The carbon atom labels have been omitted for clarity. The solid and stick bonds distinguish the two ttha moieties

(Calc.) for $C_{36}H_{87.17}Cl_{7.5}N_8Na_8Nd_2O_{70.83}$: Cl, 11.22 (10.42); Na, 6.86 (7.21); Nd, 12.32 (11.31)%].

An aqueous $[Nd(ttha)]^{3-}$ solution was also prepared for comparison of the spectral properties to those of mono- and di-meric crystals. The concentration of Nd^{III} in this solution was 4.015×10^{-2} M with a metal-to-ligand ratio of 1 : 1.2 and a final pH of 7.80.

Crystallography

A suitable crystal was cut from a larger one, placed in a capillary and mounted on a Kuma KM4 diffractometer with κ geometry and a graphite monochromator. The unit-cell parameters were determined from angular settings of 30 reflections with 2θ between 16 and 24°. The stability of data collection was monitored with three control reflections remeasured every 100 intensities. The data were corrected for Lorentz-polarization, but not for absorption or extinction. The positions of the neodymium ions were found from a Patterson map, other atoms from subsequent Fourier-difference syntheses. Owing to a large degree of disorder in this crystal not all non-hydrogen atoms (probably water oxygen atoms) could be found; the missing mass, as estimated from the difference between the measured and the calculated densities, was about 46.7 au (au $\approx 9.1 \times 10^{-31}$ kg) per asymmetric unit, equivalent to 2.6 molecules of water. The C-bonded hydrogen atoms were fixed, and no attempt to localize the O-bonded ones was made. The site occupation factors for the disordered water molecules were the maximum possible which did not cause the sum of the occupation factors of the sites located too closely to exceed 1.0. The structure was refined by full-matrix least squares on F^2 with all ordered non-hydrogen and disordered Cl(5), Cl(51), Cl(7) and Cl(71) atoms anisotropic, other disordered and hydrogen atoms isotropic. The thermal parameters of Cl(5) and Cl(51) were restrained to have the same components, as were those of Cl(7) and Cl(71). The (isotropic) thermal parameters of Cl(8) and Cl(81) were constrained to a common value. The calculations were performed with SHELXS[38] and SHELXL 93[39] programs with commonly used atom scattering factors and anomalous dispersion corrections.[40] Other details of data collection and the structure refinement are given in Table 1. All the calculated quantities from Table 1 refer to the formula defined by the atoms found from the structure analysis together with implied hydrogen atoms, *i.e.* without taking into account the missing mass.

CCDC reference number 186/838.

Spectroscopic measurements

The IR spectra of H_6ttha and mono- and di-meric crystals of Nd^{III} with ttha were recorded in the range 400–4000 cm^{-1} with a Bruker IFS 113V spectrophotometer using KBr pellets, the electronic absorption spectrum of a single crystal 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 using a spectrophotometer equipped with an Oxford CF 1204 continuous-flow cryostat at 293 and 4 K. The intensities of the 4f–4f transition (P) and values of the Ω_λ parameters were calculated from the Judd–Ofelt[41,42] relation (1) where P denotes oscillator strength, $\chi = (n^2 + 2)^2/9n$, where

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

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.*[43] and Ω_λ are empirical least-squares-fitted parameters.

Table 1 Crystallographic data for $Na_{0.5}H_{5.5}[Nd_2(ttha)_2]\cdot 7.5NaClO_4\cdot 16.83H_2O$

Empirical formula	$C_{36}H_{87.17}Cl_{7.5}N_8Na_8Nd_2O_{70.83}$
M	2503.9
T/K	298(2)
λ/Å	0.710 73
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	14.340(10)
b/Å	17.917(11)
c/Å	18.293(14)
α/°	107.66(6)
β/°	97.39(6)
γ/°	90.61(6)
U/Å^3	4435(6)
Z	2
D_m/Mg m^{-3}	1.91 (by flotation in CH_3Cl–CH_3Br)
D_c/Mg m^{-3}	1.871(2)
μ/mm^{-1}	1.56
F(000)	2523
Crystal habit	Parallelepiped
Crystal size/mm	0.3 × 0.4 × 0.5
Crystal colour	Pink-violet
Scan mode	ω–2θ
θ Range for data collection/°	2 to 25
Index ranges	$0 \leqslant h \leqslant 15$, $-21 \leqslant k \leqslant 20$, $-20 \leqslant l \leqslant 20$
Reflections collected	12 474
Reflections observed [$I \geqslant 3\sigma(I)$]	9343
Independent observed reflections	8940 ($R_{int} = 0.0247$)
Weights used, w	$1/\sigma^2(F^2)$
Data, restraints, parameters	8940, 132, 1205
Goodness-of-fit on F^2	5.629
Final R, R' indices [$I \geqslant 3\sigma(I)$]*	0.0546, 0.1355
Maximum shift/e.s.d.	0.009
Largest difference peak and hole/e Å^{-3}	+1.627, −0.950

* $R = \Sigma|F_o - F_c|/\Sigma|F_c|$; $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

Results and Discussion

Crystal structure

The geometry of the first co-ordination sphere of the neodymium(III) ions is presented in Table 2. The structure (Fig. 1) consists of the complex dimer, perchlorate anions, sodium cations and water of hydration. Both neodymium(III) ions are nine-coordinate and their environment consists of three nitrogen and six carboxylate oxygen atoms located at typical distances from the metal. The Nd(1) ··· Nd(2) distance is 7.404(6) Å, which may be compared with the shortest Nd ··· Nd separation in the related[34] monomeric compound [9.515(4) Å]. The coordinations of both Nd^{III} are essentially the same and may be defined as distorted tricapped trigonal prisms (TTPs). An alternative description in terms of capped square antiprisms (CSAs) gives slightly worse estimations of the quality of fitting. In

Table 2 Selected bond lengths (Å) and angles (°) for the $Na_{0.5}H_{5.5}[Nd(ttha)_2]\cdot 7.5NaClO_4\cdot 16.83H_2O$

Nd(1)–O(3)	2.397(8)	Nd(1)–O(19)	2.471(7)	Nd(2)–O(13)	2.415(8)	Nd(2)–O(15)	2.455(7)
Nd(1)–O(21)	2.420(7)	Nd(1)–N(7)	2.642(9)	Nd(2)–O(11)	2.431(7)	Nd(2)–N(3)	2.629(9)
Nd(1)–O(23)	2.429(8)	Nd(1)–N(8)	2.672(8)	Nd(2)–O(5)	2.445(8)	Nd(2)–N(4)	2.651(8)
Nd(1)–O(17)	2.446(7)	Nd(1)–N(6)	2.732(8)	Nd(2)–O(9)	2.445(8)	Nd(2)–N(2)	2.717(9)
Nd(1)–O(1)	2.451(7)			Nd(2)–O(7)	2.454(7)		
O(3)–Nd(1)–O(21)	79.9(3)	O(17)–Nd(1)–N(7)	65.8(3)	O(13)–Nd(2)–O(11)	83.1(3)	O(9)–Nd(2)–N(3)	92.3(3)
O(3)–Nd(1)–O(23)	78.4(3)	O(1)–Nd(1)–N(7)	137.4(3)	O(13)–Nd(2)–O(5)	139.9(3)	O(7)–Nd(2)–N(3)	123.0(3)
O(21)–Nd(1)–O(23)	127.5(3)	O(19)–Nd(1)–N(7)	122.8(3)	O(11)–Nd(2)–O(5)	136.3(3)	O(15)–Nd(2)–N(3)	136.8(3)
O(3)–Nd(1)–O(17)	142.8(3)	O(3)–Nd(1)–N(8)	73.7(3)	O(13)–Nd(2)–O(9)	77.6(3)	O(13)–Nd(2)–N(4)	72.9(3)
O(21)–Nd(1)–O(17)	136.6(3)	O(21)–Nd(1)–N(8)	64.7(2)	O(11)–Nd(2)–O(9)	127.9(3)	O(11)–Nd(2)–N(4)	64.8(3)
O(23)–Nd(1)–O(17)	72.6(3)	O(23)–Nd(1)–N(8)	63.5(3)	O(5)–Nd(2)–O(9)	71.4(3)	O(5)–Nd(2)–N(4)	112.8(3)
O(3)–Nd(1)–O(1)	80.1(3)	O(17)–Nd(1)–N(8)	111.7(3)	O(13)–Nd(2)–O(7)	75.3(3)	O(9)–Nd(2)–N(4)	63.3(3)
O(21)–Nd(1)–O(1)	141.0(2)	O(1)–Nd(1)–N(8)	138.4(3)	O(11)–Nd(2)–O(7)	70.5(2)	O(7)–Nd(2)–N(4)	127.2(3)
O(23)–Nd(1)–O(1)	80.1(3)	O(19)–Nd(1)–N(8)	128.3(2)	O(5)–Nd(2)–O(7)	118.7(2)	O(15)–Nd(2)–N(4)	139.4(3)
O(17)–Nd(1)–O(1)	72.5(3)	N(7)–Nd(1)–N(8)	69.0(3)	O(9)–Nd(2)–O(7)	144.7(3)	N(3)–Nd(2)–N(4)	69.5(3)
O(3)–Nd(1)–O(19)	73.0(2)	O(3)–Nd(1)–N(6)	133.5(3)	O(13)–Nd(2)–O(15)	79.2(3)	O(13)–Nd(2)–N(2)	137.4(3)
O(21)–Nd(1)–O(19)	71.4(2)	O(21)–Nd(1)–N(6)	78.2(2)	O(11)–Nd(2)–O(15)	140.1(3)	O(11)–Nd(2)–N(2)	78.7(3)
O(23)–Nd(1)–O(19)	142.0(3)	O(23)–Nd(1)–N(6)	145.6(3)	O(5)–Nd(2)–O(15)	72.3(3)	O(5)–Nd(2)–N(2)	71.4(3)
O(17)–Nd(1)–O(19)	118.8(2)	O(17)–Nd(1)–N(6)	73.1(3)	O(9)–Nd(2)–O(15)	82.5(3)	O(9)–Nd(2)–N(2)	142.5(3)
O(1)–Nd(1)–O(19)	70.8(2)	O(1)–Nd(1)–N(6)	92.0(2)	O(7)–Nd(2)–O(15)	70.5(2)	O(7)–Nd(2)–N(2)	62.3(3)
O(3)–Nd(1)–N(7)	140.8(3)	O(19)–Nd(1)–N(6)	61.3(2)	O(13)–Nd(2)–N(3)	141.5(3)	O(15)–Nd(2)–N(2)	90.7(3)
O(21)–Nd(1)–N(7)	73.7(3)	N(7)–Nd(1)–N(6)	68.2(3)	O(11)–Nd(2)–N(3)	74.1(3)	N(3)–Nd(2)–N(2)	68.0(3)
O(23)–Nd(1)–N(7)	95.1(3)	N(8)–Nd(1)–N(6)	129.3(3)	O(5)–Nd(2)–N(3)	65.5(3)	N(4)–Nd(2)–N(2)	129.7(3)

particular the best TTP found for Nd(1) is spanned by O(1), O(3), O(23), and N(6), O(21), N(7), which form the bases, respectively, and O(7), O(19) and N(8) forming the caps. The parameter Δ (defined as $\Sigma d_i^2/9$), $i = 1–9$, where d_i is the distance between the ith atom and the relevant vertex of the ideal least-squares-fitted polyhedron,[45] was 0.069 Å^2. The best-fitted CSA [with O(17), O(23), N(8), N(7) forming the non-capped base, O(1), O(3), O(21), N(6) the capped one, and O(19) the cap] had Δ = 0.073 Å^2. For Nd(2) the best TTP [with O(15), O(9), O(13), and N(2), N(3), O(11) as the bases, and O(7), O(5) and N(4) as the caps] had Δ = 0.056 Å^2, whereas for the best CSA [O(5), N(3), N(4), O(9) as the non-capped base, O(15), N(2), O(11), O(13) the capped one and O(7) the cap] Δ was 0.074 Å^2. The first and second co-ordination sphere (understood here as the whole of the carbon atoms which are bonded to the co-ordinated oxygen or nitrogen atoms) are practically identical, the differences being only in minor variations of the positions of the atoms with regard to the respective neodymium(III) centres. Each ttha ligand is bonded to one Nd^{III} through four of its carboxyl oxygen atoms and three of its nitrogen atoms. Two carboxyl oxygen atoms are bonded to the other Nd^{III}, and the fourth nitrogen atom remains unco-ordinated. There are nine sodium sites [of which two, Na(8) and Na(9), are half-occupied] in the asymmetric unit, each bonded to the complex anion. Atom Na(1) is bonded *via* three oxygen atoms [O(8^i), O(11^i) and O(12^i) (where i is the symmetry operation $-x, 1 - y, -z$)] to one complex moiety, whereas two Na–O bonds link it to two other ttha anions. Apart from that the Na(1) cation is bonded to a perchlorate anion and a water molecule. Atom Na(2) is held by three oxygen atoms [O(20^i), O(21^i) and O(22^i)] belonging to the same ttha anion. Apart from that the cation is bonded to O(8) and O(20), thus linking two ttha molecules belonging to the same complex $[Nd_2(ttha)_2]^{6-}$ anion. Two water molecules complete the co-ordination environment of this cation. Atom Na(3) is involved in two Na–O bonds to each of the ttha anions belonging to the same complex dimer [through atoms O(2), O(5) and O(15), O(16) respectively], two Na–OH_2 ones and a Na–O (perchlorate) interaction. The same pattern is observed for Na(4); the ttha oxygen atoms involved in this case are O(1), O(2), O(16) and O(17). In this way the last two sodium atoms seem to contribute significantly to the stabilization of the complex aggregate. Atom Na(5) forms a single bridge [between O(4) and O(22)], linking two ttha anions from the same complex ion, and is bonded to three water molecules and a perchlorate anion. Each of the other sodium cations forms only a single link to a respective ttha molecule, with the rest of the co-ordination sphere being filled by perchlorate and water oxygen atoms, many of them disordered. The structure is held together by a network of hydrogen bonds and electrostatic Na–O interactions. Some of the sodium and perchlorate ions, as well as the water molecules, are disordered.

Spectral results

The IR spectra of the monomeric $Na_3[Nd(ttha)]\cdot 2.5NaClO_4\cdot 7.617H_2O$ and dimeric $Na_{0.5}H_{5.5}[Nd_2(ttha)_2]\cdot 7.5NaClO_4\cdot 16.83H_2O$ crystals are similar but differ considerably from that of free H_6ttha. The position of the $\nu_{asym}(CO_2^-)$ band for the first crystal is 1597 cm^{-1}, while for the dimeric compound a broad band with a maximum at 1609 cm^{-1} is observed. The maximum of the $\nu_{sym}(CO_2^-)$ band is at 1409 cm^{-1} for the monomer and at 1406 cm^{-1} for the dimer. The positions of these bands compared to those of free H_6ttha indicate that carboxyl groups of the ligand in both crystals are co-ordinated.[46] Absorption at 1020–1250 cm^{-1} can be attributed to the CN group. This absorption region is rich in bands for both crystals but much less complex than for that of free H_6ttha.

The electronic absorption spectra for the two compounds are very different. A comparison between the 'hypersensitive' $^4I_{\frac{9}{2}} \longrightarrow {}^4G_{\frac{5}{2}}, {}^2G_{\frac{7}{2}}$ and the $^4I_{\frac{9}{2}} \longrightarrow {}^4F_{\frac{3}{2}}$ transitions for both crystals is given in Fig. 2. As shown previously, the monomeric crystal gives spectra very similar to those found for the $[Nd(ttha)]^{3-}$ complex in solution. The shape and splitting of absorption bands as well as the integral intensity of transitions were comparable. The positions of crystal-field components were only slightly different for these systems at room temperature.

An interesting aspect of neodymium(III) absorption involves the $^4I_{\frac{9}{2}} \longrightarrow {}^2P_{\frac{1}{2}}$ transition. Since the excited state is a Kramer's doublet and cannot be split by the ligand field, each peak in the spectrum must correspond to Stark components of the ground state. In solution, the number of the $^4I_{\frac{9}{2}} \longrightarrow {}^2P_{\frac{1}{2}}$ transition components exceeds the number of optical lines expected from group theory for Nd^{III}. This indicates that Nd^{III} has more than one environment in solution. The $^4I_{\frac{9}{2}} \longrightarrow {}^2P_{\frac{1}{2}}$ transition for the mono- and di-meric compounds and for the solution is shown in Fig. 3. A distinct nephelauxetic effect with a shift of 71 cm^{-1} towards lower energies for the dimeric crystal in relation to the monomeric one is observed. This may be caused by a change of the co-ordination number and accompanying shortening of the bond lengths. Namely, the average Nd–O distances are 2.49 and 2.44 Å for the mono- and di-meric forms, respectively, and the

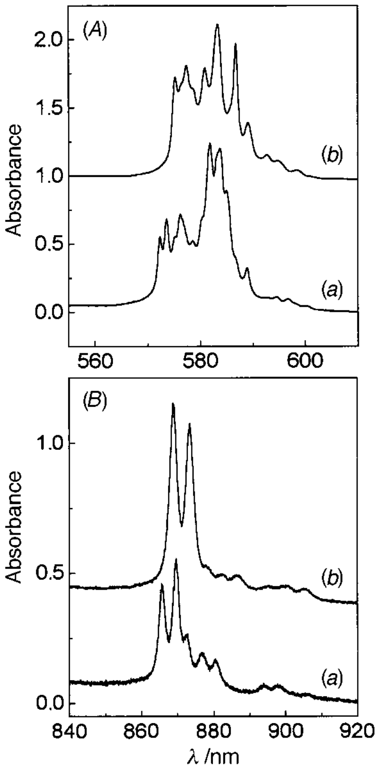

Fig. 2 Absorption spectra of the monomeric (*a*) and dimeric (*b*) single crystals at 293 K: (*A*) the 'hypersensitive' $^4I_{9/2} \longrightarrow {^4G_{5/2}}, {^2G_{7/2}}$ transition; (*B*) the $^4I_{9/2} \longrightarrow {^4F_{3/2}}$ transition. For (*a*), $c_{Nd} = 1.671$ M, $d = 0.046$ cm; for (*b*), $c_{Nd} = 1.631$ M, $d = 0.067$ cm

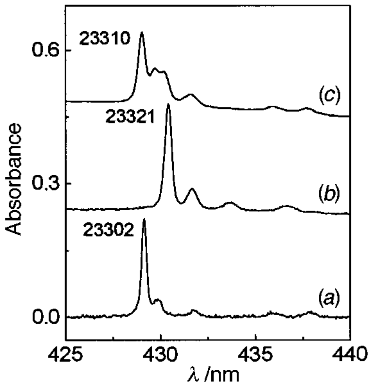

Fig. 3 Absorption spectra of the $^4I_{9/2} \longrightarrow {^2P_{1/2}}$ transition for the monomeric crystal (*a*), dimeric crystal (*b*) and solution (*c*) at 293 K. For (*a*), $c_{Nd} = 1.671$ M, $d = 0.046$ cm; for (*b*), $c_{Nd} = 1.631$ M, $d = 0.067$ cm; for (*c*), $c_{Nd} = 4.015 \times 10^{-2}$ M, pH 7.80, $d = 5$ cm

Nd–N bond lengths are 2.76 Å for the monomer and 2.68 Å for the dimer.

The splitting of the $^4I_{9/2}$ term as deduced from the $^4I_{9/2} \longrightarrow {^2P_{1/2}}$ transition for the monomeric crystal is 0, 38, 140, 356, 468 cm^{-1} and for the dimer is 0, 67, 171, 332, 407 cm^{-1}. A very similar splitting of the ground state may be obtained from the $^4I_{9/2} \longrightarrow {^4F_{3/2}}$ transition, namely 0, 37, 143, 363, 466 cm^{-1} for the monomer and 0, 58, 175, 340, 405 cm^{-1} for the dimer.

As it can be seen from Fig. 3, five components of the $^4I_{9/2} \longrightarrow {^2P_{1/2}}$ transition in solution correspond with lines of the monomeric crystal, while the position of the additional component in solution fits that of the dimeric compound. This allowed us to estimate the ratio of the monomeric species with co-ordination number 10 to the dimeric species with co-ordination number nine which exist in equilibrium in solution, $[Nd(ttha)]^{3-} : [Nd_2(ttha)_2]^{6-}$ 4:1. One cannot exclude, however, the existence of monomeric species with co-ordination number nine. In such a case there should not be a distinct change between the spectra of the centrosymmetric dimer and that of a nine-co-ordinate monomer.

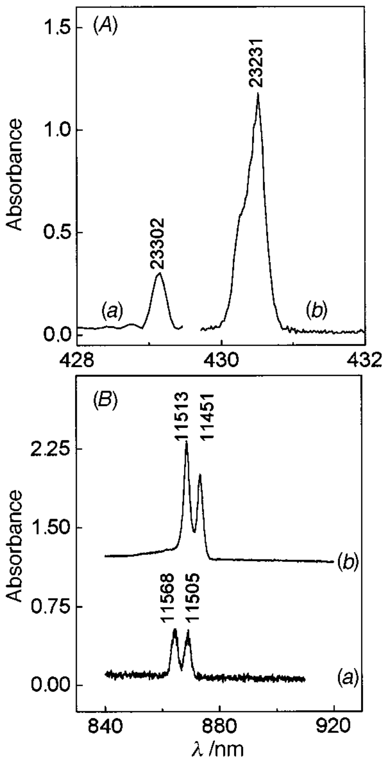

Fig. 4 Absorption spectra of the monomeric (*a*) and dimeric (*b*) single crystals at 4 K: (*A*) the $^4I_{9/2} \longrightarrow {^2P_{1/2}}$ transition; (*B*) the $^4I_{9/2} \longrightarrow {^4F_{3/2}}$ transition. For (*a*), $c_{Nd} = 1.671$ M, $d = 0.0145$ cm; for (*b*), $c_{Nd} = 1.631$ M, $d = 0.147$ cm

Table 3 Oscillator strengths (*P*) and Ω_λ parameters for the $Na_{0.5}H_{5.5}[Nd_2(ttha)_2]\cdot 7.5NaClO_4\cdot 16.83H_2O$ single crystal at 293 K

	10^8 *P*	
Transition(s) $^4I_{9/2} \longrightarrow$	exptl.	calc.
$^4F_{3/2}$	339.84	347.85
$^4F_{5/2}$, $^4H_{9/2}$	1247.52	1224.04
$^4F_{7/2}$, $^4S_{3/2}$	1307.51	1374.28
$^4F_{9/2}$	83.91	103.11
$^2H_{11/2}$	26.01	28.47
$^4G_{5/2}$, $^2G_{7/2}$	1370.38	1385.42
$^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$	951.51	748.92
$^2K_{15/2}$, $^2G_{9/2}$, $(^2D,{^2F})_{3/2}$, $^4G_{11/2}$	256.35	196.66
$^2P_{1/2}$	48.66	72.84
$^2D_{5/2}$	9.04	7.91
$^4D_{3/2}$, $^4D_{5/2}$, $^2I_{11/2}$, $^4D_{1/2}$	1425.19	1474.70
10^{20} Ω_2/cm^2	1.33 ± 0.40	
10^{20} Ω_4/cm^2	5.89 ± 0.37	
10^{20} Ω_6/cm^2	10.32 ± 0.52	
10^7 r.m.s.	8.16	

Absorption spectra of the dimeric crystal at 4 K were recorded only for a thick single crystal, because the crystal was unstable during polishing. This was a reason why transitions with low intensities could be registered at helium temperature, only. Similarly, as for the monomeric crystal, a single peak (although with a shoulder) of the $^4I_{9/2} \longrightarrow {^2P_{1/2}}$ transition and a double peak of the $^4I_{9/2} \longrightarrow {^4F_{3/2}}$ transition were found for the dimeric crystal (Fig. 4). This shows that both the neodymium(III) centres, though not strictly equivalent, are very similar.

In Table 3 the values of oscillator strengths (*P*) and the Ω_λ parameters are given. Comparing these values to those of the monomeric crystal[34] one may notice that the oscillator strength of the 'hypersensitive' $^4I_{9/2} \longrightarrow {^4G_{5/2}}, {^2G_{7/2}}$ transition is much smaller than that for the monomer. This is reflected in a decrease of the Ω_2 value. On the other hand, both the oscillator strengths and the Ω_λ values for the dimer are very close to those reported for the $K_3[Nd(nta)_2(H_2O)]\cdot 5H_2O$ crystal (H_3nta = nitrilotriacetic acid).[47] This is probably brought about by the close similarity of the chemical environments of the metal centres in both compounds.

Conclusion

In continuation of our previous studies on Nd^{III}–ttha complexes we succeeded in obtaining a dimeric compound from a solution from which the monomeric complex had been crystallized. Contrary to the monomer, the co-ordination numbers of both neodymium ions in the dimer are nine, and their environments are very similar: six carboxyl oxygen atoms and three nitrogens; one nitrogen atom of each ttha residue remains unco-ordinated. The change of co-ordination number and the chemical environment brings about a change in spectroscopic parameters of the crystal. The $^2P_{\frac{1}{2}}$ level shifts 71 cm^{-1} towards longer wavelengths, and the intensity of the 'hypersensitive' transition and the Ω_2 parameter decrease as compared with the values for the crystal of the monomer. The spectra of the solution containing a 1 : 1 metal-to-ligand ratio and at $pH > 6.0$ suggest the existence of both monomer and dimer in equilibrium.

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