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Relationships Between Structure and Spectroscopic Properties of Nd³⁺ Ethylenediaminetetramethylenephosphonates and Ethylenediaminetetraacetates

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The structural and spectroscopic properties of the Nd³⁺ compounds $[C(NH_2)_3]_7[Nd(EDTMP)(CO_3)] \cdot 10H_2O$, K₁₇H₃[Nd₄- $(EDTMP)_4]$ ·36H₂O, $[C(NH_2)_3][Nd(EDTA)(H_2O)_3]$ and $Na[Nd(EDTA)(H_2O)_3] \cdot 5H_2O$ are presented (H₄EDTA = ethylenediaminetetraacetic acid, H₈EDTMP is a phosphonic acid analogue of H₄EDTA). The obtained monomeric [Nd(EDTMP)(CO₃)]⁷⁻ and tetrameric [Nd₄(EDTMP)₄]²⁰⁻ structures, in which bidentate carbonate and tridentate bridged phosphonate coordination patterns appear, are exceptional. The use of different countercations has allowed us to assess their role in crystal formation and their influence on the spectroscopic properties of the investigated crystals. The countercations slightly change the geometry of [Nd(EDTA)-

Introduction

There is great interest in lanthanide complexes with carboxylic and phosphonic polyamino acids because of their potential applications in many areas of science. For example, the luminescent, magnetic and radioactive properties of lanthanide ions in these compounds are useful in medicine for diagnosis as well as in therapy.^[1–5] One of those compounds, a complex of radioactive ¹⁵³Sm with EDTMP (H₈EDTMP = ethylenediaminetetramethylenephosphonic acid) is used to relieve the pain caused by bone metastases.^[6] Although the complex has been applied in clinical radiotherapy since 1997, its uptake mechanism by metastatic bones is unclear.^[7,8] Therefore, it seems that a detailed investigation of the structural properties of Ln–EDTMP compounds may be helpful and could shed more light on the mechanism of drug action.

Although many structural studies of lanthanide compounds with simple mono- and bisphosphonates have been reported,^[9–11] the crystal structures of lanthanide complexes with polyamino polyphosphonic acids are rather

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 $(H_2O)_3]^-$ and some subtle modifications of the geometry of the carboxylic groups is observed. These changes are discussed in the context of hypersensitive transition intensities. The intensities of the f–f transitions in all studied crystals were determined and analyzed basing on the Judd–Ofelt theory. Luminescence of the Nd³⁺ ions in the NIR region could be observed solely in the phosphonate complexes. The luminescence quantum yields were calculated from the luminescence lifetimes and the Judd–Ofelt parameters. The ϕ value for the rigid tetramer [Nd₄(EDTMP)₄]^{20–} is twice as large (7 %) as that for the monomer [Nd(EDTMP)(CO₃)]^{7–} (3.5 %).

scarce,^[12–15] in contrast to their carboxylic analogues. The significantly larger size of the tetrahedral phosphonic group compared to the planar carboxylic group as well as its greater negative charge and basicity^[16] are the reasons why phosphonate ligands can form more diverse structures with metal cations than carboxylate ligands.^[9–11,17–19]

Our earlier structural studies on Ln^{3+} tetraphosphonates^[12–15] have revealed that the composition and geometry of the inner sphere of the Ln^{3+} ion is strongly dependent on synthesis conditions (e.g., pH, different countercations).

Therefore, in this paper we would like to report the structural and spectroscopic properties of Nd³⁺ complexes with EDTMP obtained under different experimental conditions (pH of stock solutions, different countercations). For comparison, the physicochemical properties of Nd complexes with the carboxylic analogue of EDTMP, ethylenediaminetetraacetic acid (EDTA), will be also presented.

Results and Discussion

Crystal Structures

The crystal structures of $[C(NH_2)_3]_7[Nd(EDTMP)(CO_3)]$ · 10H₂O (I), K₁₇H₃[Nd₄(EDTMP)₄]·36H₂O (II), $[C(NH_2)_3]$ -[Nd(EDTA)(H₂O)₃] (III) and Na[Nd(EDTA)(H₂O)₃]·5H₂O (IV) are briefly described. The EDTMP and EDTA ligands



coordinate to the Nd³⁺ ions in a similar way, namely, through four O and two N atoms. The remaining coordination sites are occupied by bidentate carbonate anions in I, two O atoms from an adjacent tridendate phosphonate group in II and three water molecules in III and IV. In this way, the coordination number of the Nd³⁺ ion is eight in the Nd-EDTMP complexes and nine in the Nd-EDTA complexes. Notably, in spite of the same pH (ca. 7.5) for the syntheses of II and the previously studied Eu-EDTMP complex,^[14] the tetrameric [Ln₄(EDTMP)₄]²⁰⁻ units bind different numbers of protons to yield H₃[Nd₄(EDTMP)₄]¹⁷⁻ and $H_8[Eu_4(EDTMP)_4]^{12-}$ anions. This may indicate that the Nd-EDTMP and Eu-EDTMP species are differently protonated in aqueous solution at pH ca. 7.5. Such a conclusion can be drawn from the stability constants determined potentiometrically for a series of Ln³⁺ complexes with CDTMP $[H_8CDTMP = trans-cyclohexane-1, 2-di$ amine-N, N, N', N' tetrakis(methylenephosphonic acid)].^[12]

These data indicate that the equilibria between various $[Ln(H_nCDTMP)]^{3-n}$ species differ significantly for light and heavy lanthanides. The structures of the studied complex anions are presented in Figure 1, and the Nd–L bond lengths are listed in Table 1. The data included in Table 1 demonstrate that for eight-coordinate Nd–EDTMP complexes, the average Nd–O bonds are shorter and the Nd–N bonds are longer than those of the corresponding Nd–EDTA compounds. Compounds I, III and IV contain monomeric complex anions, whereas II contains a cyclic $[Nd_4(EDTMP)_4]^{20-}$ tetramer with a cavity in the centre.

This highly negative anionic entity in II (Figure 2) shows some rigidity, which is manifested in the Nd–O bond lengths, that is, those inside the tetramer (Nd–O12ⁱ) are shorter than the outer ones (Nd–O10ⁱⁱ).

Owing to the high negative charge of $[Nd_4-(EDTMP)_4]^{20-}$, the cavity hosts H^+ and K^+ cations and water molecules. One of the K^+ cations is located in the



Figure 1. Structures of the studied complex anions. For **II**, approximately a quarter of the tetramer is shown. Only symmetry independent atoms are labelled. [a] Isostructural with $[C(NH_2)_3]_7[Eu(EDTMP)(CO_3)] \cdot 10H_2O$.^[13] [b] Isostructural with $[C(NH_2)_3]_7[Eu(EDTA) \cdot (H_2O)_3] \cdot 10H_2O$.^[13] [c] Isostructural with Na[Nd(EDTA)(H_2O)_3] \cdot 5H_2O.^[20]



Ι		II		III		IV	
Nd-O8	2.385(2)	Nd-011	2.405(4)	Nd-O3	2.412(3)	Nd-O5	2.442(3)
Nd-O1	2.407(2)	Nd-O1	2.384(5)	Nd-O4	2.420(3)	Nd-O1	2.434(3)
Nd-O10	2.407(2)	Nd-O9	2.426(5)	Nd-O1	2.467(3)	Nd-O3	2.457(3)
Nd-O6	2.438(2)	Nd-O6	2.421(4)	Nd-O2	2.482(3)	Nd-O7	2.483(3)
Nd–O _{av}	2.409(21)	Nd-O _{av}	2.409(19)	Nd–O _{av}	2.445(34)	$Nd-O_{av}$	2.454(21)
Nd-O22	2.467(2)	Nd-O12 ^{i[a]}	2.410(5)	Nd-OW1	2.468(3)	Nd-OW1	2.510(3)
Nd-O23	2.458(2)	Nd-O10 ⁱⁱ	2.545(4)	Nd-OW2	2.500(3)	Nd-OW2	2.590(3)
				Nd–OW3	2.581(3)	Nd–OW3	2.474(3)
$Nd-O_{av}$	2.463(6)	$Nd-O_{av}$	2.478(95)	Nd–OW _{av}	2.516(58)	Nd–OW _{av}	2.525(59)
Nd-N1	2.715(3)	Nd–N1	2.739(5)	Nd–N1	2.648(3)	Nd–N1	2.674(3)
Nd–N2	2.768(3)	Nd–N2	2.707(5)	Nd–N2	2.735(4)	Nd–N2	2.715(3)
Nd–N _{av}	2.742(37)	Nd-N _{av}	2.723(22)	Nd–N _{av}	2.692(62)	Nd-N _{av}	2.694(29)
Nd…Nd	10.056		6.438		7.806		6.117

Table 1. Nd–L and Nd–Nd bond lengths [Å] in Nd–EDTMP (I, II) and Nd–EDTA (III, IV).

Symmetry codes: 1 - y, x, 1 - z.



Figure 2. View of the tetrameric $[Nd_4(EDTMP)_4]^{20-}$ anion in II. The shorter inner Nd–O12ⁱ bonds are marked in red, and the longer outer Nd–O10ⁱⁱ bonds are marked in blue.

centre of the tetramer and, in this way, stabilizes the structure of the complex. The $[Nd_4(EDTMP)_4]^{20-}$ tetramers form columns and are held together by a network of hydrogen bonds and electrostatic interactions.

Inside each tetramer, a hole of diameter ca. 5.2 Å is formed. The distances between the tetrameric units are ca. 12 Å, and the neighbouring rods are ca. 15 Å away (see Scheme 1).

Notably, all the phosphonic O atoms form hydrogen bonds with $[C(NH_2)_3]^+$ ions in I, whereas only some of them interact electrostatically with K⁺ cations in II. Owing to these differences, as well as the partial protonation of $-PO_3^{2-}$ groups in II, the P–O distances are more diverse in II than in I (Table 1S).

A carbonate anion in I is also involved in a network of hydrogen bonds with some of the H_2O molecules and $[C(NH_2)_3]^+$ cations. As is shown in Scheme 2, the C20–O21 and C20–O23 bond lengths are very similar, whereas the C20–O22 bond is longer, probably because of the relatively strong hydrogen bond formed between O22 and OW3 [2.679(5) Å]. This, in turn, brings about partial withdrawal



Scheme 1. Crystal packing of II and the rods formed by the tetramers.



of the electron density from the C20–O22 bond and reduces the polarizability of the O22 atom.



Scheme 2. Geometry of the $Ln-O(CO_3^{2-})$ unit in I.

The influence of the countercations on the C–O lengths in the carboxylic groups is particularly well demonstrated in III. The coordination modes of the carboxylic groups in III and IV are presented in Scheme 3.



Scheme 3. Coordination modes of the carboxylic groups in Nd–EDTA complexes.

The elongation of the C–O (C8–O3 and C5–O4) bonds in **III** [type (b), Table 1S] is remarkable because of the simultaneous interaction of the C–O group with Nd^{3+} and $[C(NH_2)_3]^+$ cations. In particular, elongation of these bonds in **III** is a reason for the shortening of the Nd–O bonds (Nd–O3 and Nd–O4, Table 1). This effect is imperceptible for the pair of Nd³⁺ and Na⁺ cations in **IV**, as it is illustrated in Scheme 4.



Scheme 4. C-O bond lengths in III (A) and in IV (B).

The larger difference between the C–O bond lengths in III than in IV may indicate a more uniform charge distribution in the $-CO_2^-$ groups of the latter compound. This, in turn, makes the coordinated O atoms in IV somewhat more polarizable.

IR Spectroscopy

The IR spectra of the Nd compounds were recorded in the range 450–4000 cm⁻¹ (Figure 1S, Table 2S). The intense bands in the spectral range 2750–3550 cm⁻¹ with $\tilde{v}_{max} \approx$ 3400 cm⁻¹ are attributed to v(OH) vibrations from water molecules, protonated phosphonic groups in **H** as well as to

v(NH) and v(CH) oscillations. The presence of H₂O molecules coordinated to the Nd³⁺ ions in the Nd–EDTA complexes is the reason for the redshift of the v(OH) bands (ca. 30 cm⁻¹) of **III** and **IV** in comparison with those of **I** and **II**.

The most characteristic bands for the studied compounds are located in the range 870–1770 cm⁻¹. This spectral region includes bands ascribed to v(P-O), v(C-O), $\delta(CH_2)$, $\delta(OH_2)$ and $\delta(NH_2)$ vibrations. The symmetric and asymmetric v(P–O) vibrations in I and II are located at $870-1250 \text{ cm}^{-1}$. The splitting and the shape changes of the v(P-O) bands reflect the variety of P-O bonds found in the crystals. The simple structure of these bands in I is caused by the similarity of the P-O bond lengths, whereas the complex pattern in **II** is caused by the different coordination modes of the phosphonic groups as well as their protonation. The v(C–O) vibrations located at 1363 and 1462 cm^{-1} in I confirm a bidentate coordination mode of the carbonate anion, as was shown previously.^[21] The $\delta(NH_2)$ vibrations from guanidinium cations centred at 1664 cm⁻¹ in I partly cover the medium-intensity $\delta(OH_2)$ band. The band of the latter oscillations is clearly seen in the spectrum of II.

In the spectrum of III, the band between 1500–1775 cm⁻¹, which is attributed to the asymmetric v(C–O) and $\delta(NH_2)$ vibrations, is split into seven components. In this compound, two of the four carboxylic groups are engaged in hydrogen bonds with guanidinium cations. This is one of the reasons for the larger diversification of C–O bond lengths in III than in IV (Table 2S and Figure 1S), which in turn results in the intricate pattern of this band. A similar relationship may be found for the symmetric v(C–O) band, which is located at 1280–1360 cm⁻¹.

Electronic Spectroscopy

The electronic absorption spectra were measured at room and liquid helium temperatures in the spectral range 200– 2600 nm. Important information may be gained by analysis of the f–f transitions observed in this spectral region. The crystal field (CF) splitting of 4f manifolds together with the oscillator strengths of f–f transitions gives some insight into the Nd–ligand interactions. It is interesting to recognize how the various Nd³⁺ coordination environments influence the above-mentioned spectral properties.

Crystal Field Splitting

The energies of the CF components of the ${}^{4}I_{9/2}$, ${}^{4}I_{15/2}$, ${}^{4}F_{3/2}$, ${}^{4}F_{9/2}$ and ${}^{2}H_{11/2}$ multiplets, obtained from the low-temperature spectra, are presented in Table 3S.

The number of CF components is in agreement with the number predicted from group theory and indicates the low symmetry of the studied complexes. The CF splitting of the 4f levels is in general larger for the phosphonate complexes than for the carboxylate complexes. This is probably associated with the changes in the Nd–O bond lengths.

Of the f-f transitions observed in the absorption spectra of the Nd³⁺ compounds, ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$ is one of the most



suitable for the study of Nd–ligand interactions. The excited ${}^{2}P_{1/2}$ state is a Kramer's doublet and does not split in the ligand field of any symmetry. Therefore, the ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$ transition is used to study the nephelauxetic effect^[22] and for determination of the splitting of the ground ${}^{4}I_{9/2}$ state. The spectra of this transition recorded at 298 and 4.2 K are shown in Figure 3.



Figure 3. Absorption spectra of the ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$ transition. $\Delta v_{1/2} =$ 7, 16, 6 and 9 cm⁻¹ for **I**, **II**, **III** and **IV**, respectively; $\Delta v_{1/2}$ is the half-width of the ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$ band at 4.2 K.

The energies of the ${}^{2}P_{1/2}$ level of the phosphonate complexes I and II differ and are redshifted in comparison to those of the carboxylate complexes; for the latter, the respective energies are identical. Hence, the variation of the ${}^{2}P_{1/2}$ energies observed for the phosphonate complexes may be attributed to the presence of different coligands in I and **II**. The bidentate carbonate anion is more symmetrically bonded to the Nd³⁺ ion in I (Nd–O22, Nd–O23; Table 1, Scheme 2) than the tridendate bridging phosphonic group in II (Nd-O12ⁱ, Nd-O10ⁱⁱ; Table 1). For this reason, the O12ⁱ atom in the latter interacts with the Nd³⁺ cation more strongly than O10ⁱⁱ does. Such structural inequivalence gives rise to a bathochromic shift (32 cm^{-1}) of the ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$ transition relative to that of I. These data may also suggest that there is a small covalent contribution to the undoubtedly ionic Nd-ligand interaction.

From the low-temperature spectra (Figure 3), it is clear that the half-widths $(\Delta v_{1/2})$ of the ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$ bands at 4.2 K differ significantly. As the distance between neighbouring Nd ions is the shortest in **IV**, the observed slight broadening of this band in relation to that in **III** may be attributed to ion-pair interactions.^[23] A significant broadening of the ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$ band in **II** is mainly caused by the outer-sphere disorder of the H⁺ and K⁺ cations, as well as some of the water molecules.

Analysis of f-f Transition Intensities

The oscillator strengths of all f–f bands in the spectral range 320–950 nm are collected in Table 2. Although there are also f–f transitions above 950 nm in the spectra of the Nd³⁺ ions, their intensities are not included as the ${}^{4}I_{9/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}I_{9/2} \rightarrow {}^{4}I_{13/2}$ bands are superimposed with overtone and/or combination bands from organic ligands and H₂O molecules.^[24]

The intensities of all f–f transitions decrease as the temperature is reduced from 298 to 4.2 K (Table 2); this is caused by thermal depopulation of the higher CF levels of the ground ${}^{4}I_{9/2}$ state. Moreover, the oscillator strengths of

Table 2. Oscillator strengths (P) of f-f transitions and Ω_{λ} parameter values for crystals of I-IV. The P values with most influence on the Ω_2 and Ω_6 values are in *italic*.

$\overline{{}^{2}I_{9/2}} \rightarrow$	I		II		III		IV	
72	$P \times 10^{8}$	$P \times 10^8$						
	(298 K)	(4.2 K)	(298 K)	(4.2 K)	(298 K)	(4.2 K)	(298 K)	(4.2 K)
$\overline{{}^{4}D_{3/2}, {}^{4}D_{5/2}, {}^{2}I_{11/2}, {}^{4}D_{1/2}, {}^{2}L_{15/2}}$	854.5	_	893.8	900.2	1231.7	_	1133.8	5.6
² D _{5/2}	_	4.3	7.3	9.3	11.4	_	8.9	14.0
${}^{2}P_{1/2}$	20.1	11.2	32.7	34.4	47.5	16.0	28.5	18.3
${}^{2}K_{15/2}, {}^{2}G_{9/2}, ({}^{2}D, {}^{2}F)_{3/2}, {}^{4}G_{11/2}$	136.2	149.7	144.8	157.4	282.5	252.6	247.5	264.9
${}^{2}K_{13/2}, {}^{4}G_{7/2}, {}^{4}G_{9/2}$	539.5	550.2	622.3	566.8	960.7	348.9	873.3	467.6
${}^{4}G_{5/2}, {}^{2}G_{7/2}$	1789.6	942.0	1808.1	≈1480	1308.3	563.9	1645.0	≈1450
$^{2}H_{11/2}$	15.4	15.4	18.5	25.3	21.0	15.8	21.5	15.2
${}^{4}F_{9/2}$	56.0	46.2	53.8	56.2	96.6	30.8	84.0	28.0
${}^{4}F_{7/2}, {}^{4}S_{3/2}$	561.9	314.3	637.8	555.3	1204.9	345.2	1078.2	≈600
${}^{4}F_{5/2}, {}^{2}H_{9/2}$	522.4	381.0	618.5	≈610	1054.1	364.3	1013.4	≈700
${}^{4}F_{3/2}$	104.9	53.3	176.9	199.4	310.4	88.5	329.1	76.9
$\Omega_2 \times 10^{20} [\text{cm}^2]$	5.12 ± 0.23		5.03 ± 0.36		1.98 ± 0.78		3.94 ± 0.53	
$\Omega_4 \times 10^{20} [\mathrm{cm}^2]$	3.30 ± 0.21		3.52 ± 0.32		4.69 ± 0.68		4.96 ± 0.63	
$\Omega_6 \times 10^{20} [\text{cm}^2]$	4.15 ± 0.30		4.94 ± 0.47		9.49 ± 1.01		9.71 ± 0.90	
$rms \times 10^7$	8.03		4.82		18.0	-	12.5	



the most intense bands $({}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}, {}^{2}G_{7/2}, {}^{4}I_{9/2} \rightarrow {}^{4}F_{7/2}, {}^{4}S_{3/2}$ and ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}, {}^{2}H_{9/2})$ are reduced more drastically in I and III than in II and IV. This is probably because of the different interactions of organic and inorganic countercations $([C(NH_2)_3]^+$ in I and III and K⁺ and Na⁺ in II and IV) with the anionic complexes. A similar tendency was also found for Nd–TTHA (H₆TTHA = triethylenetetraamine-N, N, N', N'', N''', N'''-hexaacetic acid) compounds.^[25,26]

The intensity of the hypersensitive transition ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}, {}^{2}G_{7/2}$ is particularly affected by variations in the immediate environment of the Nd³⁺ ion; therefore, resemblance of the band shapes may reflect similar coordination environments of the Nd³⁺ ions.

The replacement of a CO_3^{2-} by a PO_3^{2-} group in Nd–EDTMP crystals gives rise to comparably shaped ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}, {}^{2}G_{7/2}$ bands and slight changes in the CF peak positions, whereas similar coordination environments of the Nd³⁺ cations in the Nd–EDTA complexes (III, IV) result in similar CF energies of the ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}, {}^{2}G_{7/2}$ transition (Figure 4). Although the countercations ([C(NH₂)₃]⁺, Na⁺) in the latter crystals do not perturb the CF energies, they do influence the intensity of the hypersensitive transition (Table 2).



Figure 4. Absorption spectra of the hypersensitive ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}, {}^{2}G_{7/2}$ transition for I–IV.

This change may be induced by a network of strong H bonds as is the case for guanidinium crystal III, contrary to the electrostatic interactions induced by the Na⁺ ions in **IV**. This, in turn, may suggest that the observed intensity changes of the hypersensitive transition are affected by the polarizability variations of the O atoms, as was discussed in the Crystal Structures section.

The Ω_{λ} intensity parameters^[27,28] are also included in Table 2. The sets of Ω_{λ} are a useful tool for comparison of f–f intensities for different systems. For example, they may be applied to find relationships between spectral and structural properties of lanthanide complexes.

For the Nd–EDTA crystals, the constant values of the Ω_4 and Ω_6 parameters may reflect the same Nd³⁺ coordination environments in **III** and **IV**, whereas significant variations in the Ω_2 values may indicate the influence of the ligand polarizability mechanism on this parameter. Such interpretation is consistent with the study by Mason and Tranter on lanthanide tetrakis(dithiocarbamates).^[29,30] They showed that the ligand polarizability contributes to the Ω_{λ} values by 66, 17 and 0.1% for $\lambda = 2, 4, 6$, whereas the corresponding CF contributions increase from 5 to 57 to 98.5%, respectively.

For the Nd–EDTMP crystals (I and II), for which the symmetry of the Nd³⁺ environment is nearly the same, the oscillator strengths of the hypersensitive transition as well as the respective Ω_4 and Ω_6 values are comparable. Therefore, it is puzzling that coligands with different oxygen atom polarizabilities ($a_{\rm C-O} = 3.85 \text{ Å}^3$, $a_{\rm P-O} \approx 1.4 \text{ Å}^3$)^[31] give similar Ω_2 parameter values in I and II.

It seems that such coincidence of Ω_2 values is rather accidental by taking into account the results obtained for the Nd–EDTA crystals as well as for the more complicated Nd–TTHA system.^[25,26] A possible explanation is as follows. In Nd–EDTA and Nd–TTHA compounds, the guanidinium countercation, contrary to the Na⁺ one, is engaged in hydrogen bonds with some O atoms, coordinated to the Nd³⁺ cation, which results in some reduction of electron density in the C–O bonds and decreases the polarizability of the respective O atoms, as was discussed in the Crystal Structure section.

Therefore, assuming a similar influence of the guanidinium cation on the O atoms from the CO_3^{2-} anion in I, one may expect that the replacement of $[\text{C}(\text{NH}_2)_3]^+$ by an inorganic cation should result in an increase in the Ω_2 parameter. An inspection of the spectra (Figure 5) and Ω_{λ} parameters for the Nd–EDTMP and Nd–EDTMP–CO₃ complexes in aqueous solutions (Table 3) together with those



Figure 5. Absorption spectra of the ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$ (A) and hypersensitive ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$, ${}^{2}G_{7/2}$ (B) transitions for crystals of I and Nd–EDTMP complexes at various pH values.



for crystals of I (Table 2) is helpful to assess the influence of coligands on the Ω_{λ} parameter. The solutions of Nd–EDTMP at pH 9.1 and 10.7 were adjusted with NaOH, and the Nd–EDTMP–CO₃ solution at pH = 10.7 was adjusted with [C(NH₂)₃]₂CO₃ (I was obtained under similar experimental conditions).

Table 3. Oscillator strengths ($P \times 10^8$) of the f–f transitions and Ω_{λ} parameter values for Nd–EDTMP in solutions at different pH values.

$^{2}I_{9/2} \rightarrow$	pH = 10.7 [C(NH ₂) ₃] ₂ CO ₃	pH = 10.7 NaOH	pH = 9.1 NaOH
$^{4}D_{3/2}, ^{4}D_{5/2}, ^{2}I_{11/2},$	865.5	809.9	762.9
${}^{4}D_{1/2}, {}^{2}L_{15/2}$			
$^{2}D_{5/2}$	4.6	5.5	5.2
${}^{2}P_{1/2}$	30.1	30.7	31.6
${}^{2}\mathrm{K}_{15/2}, {}^{2}\mathrm{G}_{9/2},$	148.7	146.6	143.8
$(^{2}\text{D}, ^{2}\text{F})_{3/2}, ^{4}\text{G}_{11/2}$			
${}^{2}K_{13/2}, {}^{4}G_{7/2}, {}^{4}G_{9/2}$	629.2	499.2	500.5
${}^{4}G_{5/2}, {}^{2}G_{7/2}$	2251.9	1005.6	1013.5
$^{2}H_{11/2}$	15.6	14.5	14.8
${}^{4}F_{9/2}$	57.5	51.7	54.4
${}^{4}F_{7/2}, {}^{4}S_{3/2}$	672.6	734.8	736.2
${}^{4}F_{5/2}, {}^{2}H_{9/2}$	703.5	748.3	751.9
${}^{4}F_{3/2}$	166.7	199.8	198.9
$\Omega_2 \times 10^{20} [\rm cm^2]$	7.85 ± 0.26	2.09 ± 0.32	2.27 ± 0.36
$\Omega_4 \times 10^{20} [\rm cm^2]$	3.70 ± 0.23	3.52 ± 0.29	3.29 ± 0.33
$\Omega_6 \times 10^{20} [{\rm cm}^2]$	6.05 ± 0.33	6.73 ± 0.42	6.81 ± 0.47
$rms \times 10^7$	6.00	5.84	6.50

The remarkable agreement between the spectra of I and the Nd–EDTMP–CO₃ solution (Figure 5) may suggest that the coordination geometry of $[Nd(EDTMP)(CO_3)]^{7-}$ species in solution is similar to that found in I.

However, the Ω_2 and Ω_6 values are higher for the [Nd(EDTMP)(CO₃)]^{7–} complex in solution than those for crystals of I (Table 2). This should not be surprising, as the [Nd(EDTMP)(CO₃)]^{7–} species in solution are in dynamic equilibrium and the determined Ω_{λ} parameters are averaged.

It is worth checking how variously polarizable coligands will affect the values of the Ω_{λ} parameter. The hydroxy species described by the following simplified reaction are in equilibrium in Ln–EDTMP solutions at pH above 9 alkalized by NaOH:^[13,32]

 $[Nd(EDTMP)(H_2O)_2]^{5-} + OH^- \leftrightarrow \\ \leftrightarrow [Nd(EDTMP)(H_2O)(OH)]^{6-} + H_2O$

From DFT calculations, the symmetry of these species as well as that of $[Nd(EDTMP)(CO_3)]^{7-}$ are substantially the same.^[33,34] The Ω_4 values determined for all studied solutions and crystals of I are constant, whereas the Ω_6 values are similar only for the solutions. This may suggest that the CF potential mostly contributes to the Ω_6 parameter. In turn, different coligand polarizabilities ($a_{H_2O} = 1.442 \text{ Å}^3$, $a_{OH^-} = 2.03 \text{ Å}^3$, $a_{CO_3^{2-}} = 3.85 \text{ Å}^3$)^[31,35] mainly influence the Ω_2 parameter values.

Luminescence Properties

The ${}^{4}F_{3/2} \rightarrow {}^{4}I_{J'}$ (J' = 9/2, 11/2, 13/2, 15/2) emission of Nd³⁺ ions in complexes with organic ligands is usually quenched by the high-energy vibrations of OH, NH and

CH groups from the ligand and solvents. This is one of the reasons for low luminescence intensity and short lifetimes (a few μ s) in these compounds, especially in solutions.

By exciting Nd^{3+} ions at 514.5 nm, the near-IR (NIR) luminescence spectra could be recorded for the phosphonate crystals, only. The emission spectra of I and II are presented in Figure 6.



Figure 6. Emission spectra ($\lambda_{ex} = 514.5 \text{ nm}$) of Nd–EDTMP crystals.

The relative intensities of the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{J'}$ bands are stronger in II than in I. Based on the determined Ω_{λ} values (Table 2), the spontaneous emission probabilities $A({}^{4}F_{3/2} \rightarrow {}^{4}I_{J'})$, luminescence branching ratios $\beta({}^{4}F_{3/2} \rightarrow {}^{4}I_{J'})$ and the radiative lifetimes were calculated and are given in Table 4, in which the τ_{exp} and quantum yield (Φ) are also included.

Table 4. Luminescence parameters for the studied crystals.

	Ι	II	III	IV
$\overline{\Omega_4/\Omega_6}$	0.80	0.71	0.50	0.51
$A({}^{4}\mathrm{F}_{3/2} \rightarrow {}^{4}\mathrm{I}_{9/2}) [\mathrm{s}^{-1}]$	824	898	1301	1362
$A({}^{4}\mathrm{F}_{3/2} \rightarrow {}^{4}\mathrm{I}_{11/2})[\mathrm{s}^{-1}]$	1027	1187	2118	2178
$A({}^{4}\mathrm{F}_{3/2} \rightarrow {}^{4}\mathrm{I}_{13/2}) [s^{-1}]$	209	246	434	445
$A({}^{4}\mathrm{F}_{3/2} \rightarrow {}^{4}\mathrm{I}_{15/2}) [\mathrm{s}^{-1}]$	9	11	20	20
$\beta({}^{4}\mathrm{F}_{3/2} \rightarrow {}^{4}\mathrm{I}_{9/2})$	0.398	0.384	0.336	0.340
$\beta({}^{4}\mathrm{F}_{3/2} \rightarrow {}^{4}\mathrm{I}_{11/2})$	0.497	0.507	0.547	0.544
$\beta({}^{4}\mathrm{F}_{3/2} \rightarrow {}^{4}\mathrm{I}_{13/2})$	0.101	0.105	0.112	0.111
$\beta({}^{4}\mathrm{F}_{3/2} \rightarrow {}^{4}\mathrm{I}_{15/2})$	0.004	0.004	0.005	0.005
$\tau_{\rm R}$ [µs]	483	427	258	250
$\tau_{\rm exp}$ [µs]	18	31	_	_
Φ [%]	3.7	7.2	_	_

For Nd³⁺ ions, the luminescence parameters determined from the Judd–Ofelt analysis depend on the Ω_4 and Ω_6 values only, as the square matrix elements U(2) for the ${}^4F_{3/2} \rightarrow {}^4I_{J'}$ transitions are equal to zero. The calculated spontaneous emission coefficients $A({}^4F_{3/2} \rightarrow {}^4I_{J'})$ and branching ratios $\beta({}^4F_{3/2} \rightarrow {}^4I_{J'})$ suggest that Nd–EDTA complexes should be better NIR emitters than Nd– EDTMP crystals.

However, the determined rates $(1/\tau_R)$ do not include non-radiative processes, which are more effective for the carb-



oxylates owing to the presence of three water molecules in the first coordination sphere of the Nd^{3+} ions.

More effective luminescence quenching in I than in II is caused by the presence of CO vibrations from the coordinated carbonate anion as well as high-energy v(NH) oscillations from the guanidinium cations. The energy of the v(CO) vibrations is about 400 cm⁻¹ higher than that from the PO group (Table 2S). For II, τ_{exp} is probably partially reduced by ion-pair interactions, as the Nd–Nd distance is much shorter in II (6.438 Å) than in I (10.056 Å).

The Judd–Ofelt analysis of the absorption spectra, together with the experimentally determined lifetimes, allowed us to calculate luminescence quantum yields for the studied crystals; it should be stressed that it is rare to use such a method to determine Φ for NIR-luminescent lanthanide complexes with organic ligands.

The obtained quantum yield is two times higher for **II** than for **I** and probably should be associated with the rigidity of the tetrameric $[Nd_4(EDTMP)_4]^{20-}$ units. To the best of our knowledge, the Φ value of 7.2% for **II** is one of the highest reported to date for Nd³⁺ chelates.^[36]

It is also notable that evaluation of radiative lifetimes for Nd³⁺ compounds with organic ligands is not straightforward; it is usually assumed that the τ_R value is constant and taken from the literature ($\tau_R = 270 \ \mu s$ for Y₂O₃:Nd).^[37] Our results suggest that this crude assumption is unjustified, as the τ_R values strongly depend on the chemical environment of the Nd³⁺ cation.

Conclusions

In this paper, a detailed analysis of the physico-optical properties of $[C(NH_2)_3]_7[Nd(EDTMP)(CO_3)] \cdot 10H_2O$, $K_{17}H_3[Nd_4(EDTMP)_4]$ ·36 H_2O , [C(NH₂)₃][Nd(EDTA)-(H₂O)₃] and Na[Nd(EDTA)(H₂O)₃]·5H₂O was performed. Both ligands, EDTMP and EDTA, coordinate to the Nd³⁺ ion through two N and four O atoms. The remaining coordination sites are occupied by two O atoms from a bidentate CO₃²⁻ or tridendate PO₃²⁻ group in the Nd–EDTMP complexes (I and II) and three H₂O molecules in the Nd-EDTA complexes (III and IV). The coordination number of the Nd³⁺ ions in the Nd–EDTMP complexes (CN = 8) is one less than that in the Nd-EDTA compounds (CN = 9). The complex anions in I, III and IV are monomeric, whereas cyclic [Nd₄(EDTMP)₄]²⁰⁻ tetramers are formed in II. Inside each tetramer, a hole is formed, which is filled with water molecules, as well as H⁺ and K⁺ cations. The cations stabilize the highly negative supramolecular units.

Monomeric and tetrameric coordination patterns are very rare for lanthanide complexes with polyphosphonic ligands. Moreover, the coordination of a CO_3^{2-} anion to a highly negative lanthanide chelate, such as that found in I, is also very uncommon. In such chelate compounds, H₂O and/or OH⁻ coligands usually complete the inner spheres of the metal cations.^[12] The bidentate coordination mode of the carbonate anion in I is caused by a good fit of this ion to the coordination geometry of the [Nd(EDTMP)]⁵⁻ unit.

The use of different organic $\{[C(NH_2)_3]^+\}$ and inorganic (K⁺/Na⁺) countercations has enabled us to observe their role in crystal formation as well as their influence on the spectroscopic properties of the investigated crystals. The geometry of the Nd-EDTA complex in both crystals is practically the same, as indicated by the X-ray data and the CF splitting of the 4f manifolds. Therefore, the observed intensity changes of the hypersensitive transition in the spectra of **III** and **IV** are attributed to ligand polarizability variations. Indeed, some of the C-O bonds in III are significantly elongated owing to the simultaneous interactions of CO groups with Nd³⁺ and guanidinium cations. Such elongation results in greater separation of the electron cloud around the shifted O atom from the rest of the carboxylic group. This, in turn, results in a decrease of the atom polarizability. In this way, it is possible to trace the impact exerted by fine modifications of the structure on the hypersensitive transition intensities. The influence of ligand polarizability and symmetry on the \varOmega_2 and \varOmega_6 values, respectively, was also shown for Nd-EDTMP complex solutions and crystals.

The calculated Ω_{λ} parameters enabled us to retrieve the spontaneous emission coefficients $A({}^{4}F_{3/2} \rightarrow {}^{4}I_{J'})$ and branching ratios $\beta({}^{4}F_{3/2} \rightarrow {}^{4}I_{J'})$. These data suggested that the Nd-EDTA crystals should be better NIR emitters than the Nd-EDTMP complexes. Therefore, the luminescence properties of the crystals were examined. Unfortunately, owing to the presence of three water molecules in the vicinity of the metal cation in the EDTA complexes, the NIR emission is efficiently quenched by v(OH) oscillations. The lack of water molecules in the nearest environment of the Nd³⁺ ions in the EDTMP crystals is a reason for the good luminescence properties of crystals of I and II. To check the efficiency of the luminescence processes in both phosphonic compounds, the quantum yields were estimated. These parameters were determined based on the Judd-Ofelt parameters. The Φ value calculated for II (7.2%) is approximately twice as high as that determined for I and is one of the highest reported to date for Nd³⁺ chelates. This result suggests that polymeric coordination compounds have better luminescent properties than monomers. It was also shown that the radiative luminescence lifetime for Nd³⁺ compounds with organic ligands depends on the Nd³⁺ environment.

Experimental Section

Crystal Syntheses: Crystals of the Nd–EDTMP complexes were prepared as follows. Equimolar quantities of Nd₂O₃ (99.9%, MERCK; 4 mmol) and solid H₈EDTMP (95%, ABCR; 8 mmol) were mixed together and heated at 90 °C (\pm 5 °C) for ca. 3 d. Next, the mixtures were alkalized with [C(NH₂)₃]₂CO₃ (Aldrich) or KOH (POCH) to adjust the pH of the solutions to 10.7 or 7.5, respectively. After slow evaporation of these aqueous solutions (ca. 25 mL), violet crystals of [C(NH₂)₃]₇[Nd(EDTMP)(CO₃)]·10H₂O (I) and K₁₇H₃[Nd₄(EDTMP)₄]·36H₂O (II) were obtained.

Crystals of the Nd–EDTA complexes were prepared in the following way. A stock solution of $NdCl_3$ was obtained by dissolving



 Nd_2O_3 (99.9%, MERCK) in 2 M HCl. The metal concentration was determined complexometrically by using xylenol orange as the indicator. To the aqueous solution of NdCl₃ (2 mmol), a solution of H₄EDTA (2 mmol) was added. The resulting solution was alkalized with [C(NH₂)₃]₂CO₃ (Aldrich) or NaOH (POCH) to pH 10.5. During slow evaporation of the solution (ca. 25 mL), crystals of [C(NH₂)₃][Nd(EDTA)(H₂O)₃] (III) and Na[Nd(EDTA)(H₂O)₃]· 5H₂O (IV) formed.

X-ray Analyses: Suitable single crystals were cut from larger ones, mounted in a Kuma KM4 diffractometer equipped with a CCD detector and measured at 100 K (I and II) and room temperature (III and IV). The structures were solved routinely by using a Patterson synthesis. The C- and N-bonded hydrogen atoms were placed in positions calculated from the geometry, and most of those bonded to O atoms were found from difference Fourier maps. The final refinements were anisotropic for all non-H atoms. The computations were performed with the SHELXS97^[38] and SHELXL97^[39] programs, and the molecular graphics were prepared with XP-Interactive Molecular Graphics.^[40]

Selected Crystal Data for I: $C_{14}H_{74}NdN_{23}O_{25}P_4$, M = 1240.80, monoclinic, space group P_{21}/n , T = 100 K, Z = 4, a = 12.428(4), b = 16.615(6), c = 24.066(9) Å, $\beta = 101.58(3)^\circ$, V = 4868(3) Å³, $\mu = 1.30$ mm⁻¹, D = 1.682 g/cm³, F(000) = 2556, crystal size $= 0.3 \times 0.4 \times 0.25$ mm, $\theta = 3-28.5^\circ$, index ranges: $-16 \le h \le 12, -21 \le k \le 22, -30 \le l \le 32$, reflections collected/unique = 31261/11207 ($R_{int} = 0.0728$). Final R indices $[I > 2\sigma(I)] R(F) = 0.0420$, $R_w(F^2) = 0.0581$ and R(F) = 0.0936, $R_w(F^2) = 0.0638$ (all data), data completeness to $2\theta = 28.5^\circ$, 92.1%, largest diff. peak and hole 0.557 and -0.720 eÅ⁻³.

Selected Crystal Data for II: $C_{6}H_{30.75}K_{4.25}N_2NdO_{21}P_4$, M = 901.37, tetragonal, space group $P\overline{42}$, T = 100 K, Z = 4, a = 21.7012(6), b = 12.5981(6), V = 5933.0(4) Å³, $\mu = 1.30$ mm⁻¹, D = 2.018 g/cm³, F(000) = 3596, crystal size $= 0.15 \times 0.13 \times 0.2$ mm, $\theta = 3-28.5^{\circ}$, index ranges: $-16 \le h \le 12$, $-21 \le k \le 22$, $-30 \le l \le 32$, reflections collected/unique = 39254/7147 ($R_{int} = 0.0755$). Final R indices $[I > 2\sigma(I)] R(F) = 0.0451$, $R_w(F^2) = 0.1183$ and R(F) = 0.1211, $R_w(F^2) = 0.0532$ (all data), data completeness to $2\theta = 28.5^{\circ}$, 95.71%, largest diff. peak and hole 1.333 and -1.758 eÅ⁻³.

Selected Crystal Data for III: $C_{11}H_{24}NdN_5O_{11}$, M = 546.64, monoclinic, space group $P2_1/c$, T = 293 K, Z = 4, a = 11.270(5), b = 8.662(4), c = 18.736(9) Å, $\beta = 90.09(4)^\circ$, V = 1829.0(15) Å³, $\mu = 2.908$ mm⁻¹, D = 1.985 g/cm³, F(000) = 1092, crystal size $= 0.4 \times 0.17 \times 0.1$ mm, $\theta = 3-28.5^\circ$, index ranges: $-16 \le h \le 12, -21 \le k \le 22, -30 \le l \le 32$, reflections collected/unique = 15796/4472 ($R_{int} = 0.0227$). Final R indices $[I > 2\sigma(I)] R(F) = 0.0299$, $R_w(F^2) = 0.0819$ and R(F) = 0.0829, $R_w(F^2) = 0.0352$ (all data), data completeness to $2\theta = 28.5^\circ$, 93.4%, largest diff. peak and hole 1.770 and -1.740 eÅ⁻³.

Selected Crystal Data for IV: $C_{10}H_{28}NdN_2O_{16}Na$, M = 599.63, orthorhombic, space group Fdd2, T = 293 K, Z = 4, a = 19.5430(3), b = 35.4950(5), c = 12.0585(2) Å, V = 8364.7(2) Å³, $\mu = 2.584$ mm⁻¹, D = 1.904 g/cm³, F(000) = 4816, crystal size $= 0.2 \times 0.31 \times 0.16$ mm, $\theta = 3-25^{\circ}$, index ranges: $-22 \le h \le 23$, $-42 \le k \le 42$, $-14 \le l \le 14$, reflections collected/unique = 24708/3679 ($R_{int} = 0.0242$). Final R indices [$I > 2\sigma$ (I)] R(F) = 0.0197, $R_w(F^2) = 0.0521$ and R(F) = 0.0524, $R_w(F^2) = 0.0206$ (all data), data completeness to $2\theta = 25.1^{\circ}$, 99.6%, largest diff. peak and hole 1.15 and -0.70 eÅ⁻³.

CCDC-920543 (for I), -920541 (for II), -920544 (for III) and -920542 (for IV) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Spectroscopic Measurements: IR spectra of the complexes in KBr pellets and nujol suspensions were measured in the range 50–4000 cm⁻¹ with a Bruker FTIR IFS66 spectrometer. Electronic absorption spectra were recorded with a Cary 500 UV/Vis/NIR spectrophotometer equipped with an Oxford Optistat continuous flow helium cryostat for crystal measurements at 4.2 K. Luminescence spectra in the NIR region were measured at room temperature with a Dongwoo (model DM711) scanning monochromator with 750 mm focal length equipped with an InGaAs detector. The Nd³⁺ ions in the studied crystals were excited by an Ar ion laser operating at $\lambda = 514.5$ nm. Luminescence decay curves were recorded with a Tektronix (model TDS 3052) digital oscilloscope. Excitation was provided by a continuum optical parametric oscillator (OPO) pumped by the third harmonic of an YAG:Nd laser ($\lambda = 355$ nm).

Calculations: The intensities of f-f transitions were determined in terms of oscillator strengths (P) by numerical integration of the corresponding absorption bands by using the formula [Equation (1)]

$$P = \frac{4.33 \cdot 10^{-9}}{c \cdot d} \int A(\tilde{v}) \, \mathrm{d}\tilde{v} \tag{1}$$

in which *c* is the concentration of the Nd³⁺ ion in M, *d* is the length of the optical path in cm and $A(\tilde{v})$ is the absorbance as a function of the wavenumber \tilde{v} in cm⁻¹.

The experimental *P* values were used to calculate the phenomenological Ω_{λ} intensity parameters according to the Judd–Ofelt relation [Equation (2)]

$$P_{\rm ED} = \chi \frac{8\pi^2 m c \tilde{\nu}}{3h(2J+1)} \sum_{\lambda=2,4,6} \Omega_{\lambda} \left| \left\langle \Psi' J' \right\| U^{(\lambda)} \left\| \Psi J \right\rangle \right|^2$$
(2)

in which $P_{\rm ED}$ is the oscillator strength of the electric dipole transition, $\chi = (n^2 + 2)^2/9n$, *n* is the refractive index, *m* is the electron mass, *c* is the speed of light, \tilde{v} is the wavenumber of the band maximum in cm⁻¹, *h* is the Planck constant, *J* is the ground state quantum number, $\langle \psi' J' || U^{(\lambda)} || \psi J \rangle$ are the reduced matrix elements of the respective unit tensor operator $U^{(\lambda)}$. The $\langle || U^{(\lambda)} || \rangle^2 = U(\lambda)$ values were calculated and tabulated by Carnall et al.^[41]

A measure of the accuracy of the fit intensity parameters was given by the root mean square deviation (rms) of the experimental and calculated [from Equation (2)] oscillator strengths by the following Equation (3)

rms =
$$\sqrt{\sum_{i=4}^{n} (P_{exp}^{(i)} - P_{cal}^{(i)})^2 / (n-3)}$$
 (3)

in which n is the number of absorption bands and 3 is the number of fitting parameters.

The calculated Ω_{λ} intensity parameters were used to evaluate the radiative transition rates $A(\psi J, \psi' J')$ for electric dipole transitions between an excited state and the lower lying levels, luminescence branching ratios $\beta(\psi J, \psi' J')$ and radiative decay time $\tau_{\rm R}$ from Equations (4), (5) and (6)



$$A(\psi \mathbf{J}, \psi' \mathbf{J}') = \frac{64\pi^2 e^2 \tilde{v}^3}{3h(2\mathbf{J}+1)} \left[\frac{n(n^2+2)^2}{9} \right]_{\lambda=2,4,6} \Omega_{\lambda} \left| \left\langle \psi' \mathbf{J}' \right\| \mathbf{U}^{(\lambda)} \left\| \psi \mathbf{J} \right\rangle \right|^2$$
(4)

$$\beta(\psi \mathbf{J}, \psi' \mathbf{J}') = \frac{A(\psi \mathbf{J}, \psi' \mathbf{J}')}{\sum_{J} A(\psi \mathbf{J}, \psi' \mathbf{J}')}$$
(5)

$$\tau_{\rm R} = \frac{1}{\sum_{\rm J} A(\psi {\rm J}, \psi' {\rm J}')}$$
(6)

in which *e* is the electron charge and the other symbols are the same as those in Equation (2). The $\tau_{\rm R}$ together with the experimental luminescence lifetimes ($\tau_{\rm exp}$) were used to calculate the quantum yield

$$\Phi = \frac{\tau_{\exp}}{\tau_{\rm R}} \cdot 100\%.$$

Supporting Information (see footnote on the first page of this article): selected bond lengths of CO_2^- and PO_3^{2-} groups, IR frequencies and IR spectra, energies of CF levels for the Nd³⁺ ions in crystals of I–IV.

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