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Syntheses and Crystal Structures of the Cyclotriphosphate Hydrates $Nd(P_3O_9)·3H_2O$, $Nd(P_3O_9)·4.5H_2O$, $RE(P_3O_9)·5H_2O$ (*RE* = Pr, Nd), and $Na_3RE(P_3O_9)_2·6H_2O$ (*RE* = Pr, Nd)

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Keywords: Phosphate; Hydrates; Crystal structure; Rare-earth; Vibrational spectroscopy

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Abstract. Several rare-earth cyclotriphosphate hydrates were obtained from mixtures of sodium cyclotriphosphates and the respective rare-earth chlorides. $Nd(P_3O_9)·3H_2O$ [$P\bar{6}$, $Z = 3$, $a = 677.90(9)$, $c = 608.67(9)$ pm, $R_1 = 0.016$, $wR_2 = 0.038$, 312 data, 36 parameters] was obtained by a solid state reaction and is isotypic with respective rare-earth phosphate hydrates, while all the others adopt new structure types. $Nd(P_3O_9)·4.5H_2O$ [$C2/c$, $Z = 8$, $a = 1644.6(3)$, $b = 756.11(15)$, $c = 1856.1(4)$ pm, $\beta = 97.25(3)°$, $R_1 = 0.032$, $wR_2 = 0.081$, 1763 data, 194 parameters], $Nd(P_3O_9)·5H_2O$ [$P2_1/c$, $Z = 4$, $a = 773.75(15)$, $b = 1149.1(2)$, $c = 1394.9(3)$ pm, $\beta = 106.07(3)°$, $R_1 = 0.042$, $wR_2 = 0.082$, 1338 data, 194 parameters], $Pr(P_3O_9)·5H_2O$ [$P\bar{1}$, $Z = 2$, $a = 745.64(15)$, $b = 889.07(18)$, $c = 934.55(19)$ pm, $\alpha = 79.00(3)$, $\beta = 80.25(3)$, $\gamma = 66.48(3)$, $R_1 = 0.059$, $wR2 = 0.089$, 1468 data, 193 parameters], $Na_3Nd(P_3O_9)_2·6H_2O$ [$P2_1/n$, $Z = 4$, $a = 1059.78(18)$, $b = 1207.25(15)$, $c = 1645.7(4)$ pm, $\beta = 99.742(17)$, $R_1 = 0.047$, $wR_2 = 0.119$, 1109 data, 351 parameters] and $Na_3Pr(P_3O_9)_2·6H_2O$ [$P2_1/n$, $Z = 4$, $a = 1061.42(16)$, $b = 1209.0(2)$, $c = 1635.5(3)$ pm, $\beta = 99.841(13)$, $R_1 = 0.035$, $wR_2 = 0.062$, 1323 data, 350 parameters] were obtained by careful crystallization at room temperature. A thorough structure discussion is given. The infrared spectrum of $Nd(P_3O_9)·4.5H_2O$ is also reported.

Introduction

Phosphate chemistry is very versatile as there exist besides a large number of non-hydrated cyclophosphates[1] also orthophosphates like $BaHPO_4$,[2,3] oligophosphates like Trömelite $Ca_4P_6O_{19}$,[4] catenaphosphates like $Sr(PO_3)_2$,[5–8] and ultraphosphates. Besides the rare-earth cyclotriphosphate hydrates we intend to focus on in this contribution, also quite a lot light has already been shed on the crystal structure determination of hydrated species of the commonly known cyclotriphosphates like the recently published $MnK_4(P_3O_9)·2.2H_2O$ and $SrKP_3O_9·3H_2O$.[9,10] Analogous rare-earth compounds structurally described are the trihydrates $RE(P_3O_9)·3H_2O$ (*RE* = La, Ce, Pr),[11–14] and heavily hydrated mixed cyclotriphosphate hydrates $Na_3M(P_3O_9)·9H_2O$ (*M* = Y, Bi,[15] Sm – Er,[13,16] Yb[17]). Frequently, syntheses of assumed hydrates and their dehydration behavior were published without any structural investigation. As an example we mention contributions on the preparation as well as the thermal behavior on powder samples of cerium cyclotriphosphate hydrate $Ce(P_3O_9)·3H_2O$,[18] neodymium cyclotriphosphate hydrates of the assumed composition $Nd(P_3O_9)·4H_2O$,[19] and $Nd(P_3O_9)·5H_2O$[20] without giving any crystal structure information and structure suggestions based on vibrational spectroscopy only.

In the course of our structural investigations to have a closer look on these investigations we identified a series of new rare-earth cyclotriphosphate hydrates, which we will focus on in this contribution. With one exception all of them represent new structure types. It should be mentioned that the preparation of such hydrates aside from the very stable tri- and nonahydrates is tricky, the handling of the single-crystals not trivial and phase-pure powders can only be obtained occasionally.

Results and Discussion

Crystal Structure of $Nd(P_3O_9)·3H_2O$

$Nd(P_3O_9)·3H_2O$ adopts space group $P\bar{6}$ and crystallizes isotypically with $RE(P_3O_9)·3H_2O$ (*RE* = La, Ce, Pr).[9–12] The neodymium atoms are arranged as hexagonal rod packing with crystal water molecules and cyclotriphosphate anions in the resulting channels (Figure 1). All water molecules coordinate the trivalent neodymium atoms.

The Nd^{3+} cations are coordinated by nine oxygen atoms with six from terminal oxygen atoms of the cyclotriphosphate anions forming a trigonal prism, and together with further three oxygen atoms of the water molecules a tricapped trigonal

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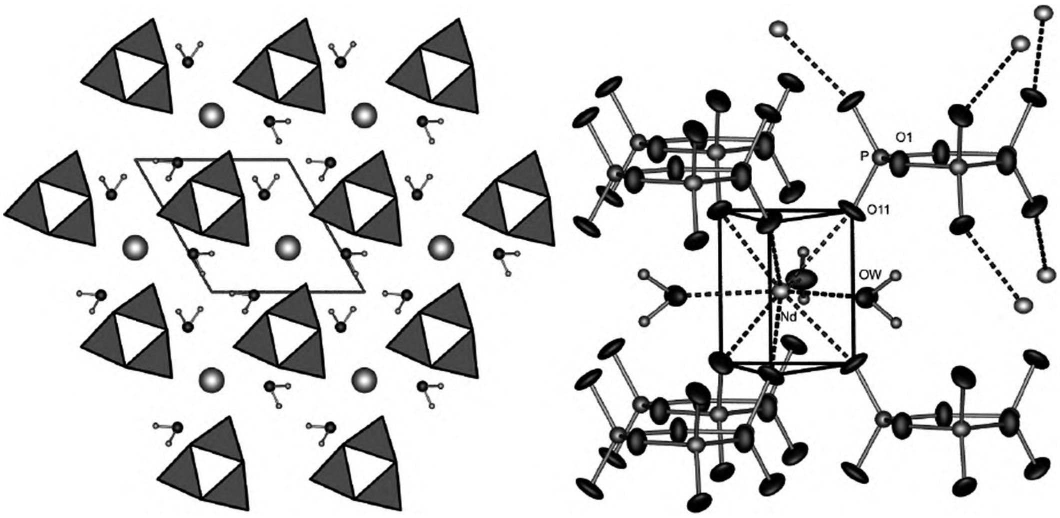

Figure 1. Crystal structure viewed along [001] and coordination of the neodymium atoms in $Nd(P_3O_9)\cdot 3H_2O$, the displacement ellipsoids are drawn on a probability level of 50 %.

prism is obtained (Figure 1). The distances Nd–O range from 251.5(3) for the terminal oxygen till 258.7(5) pm for the crystal water molecules. These values are in very good agreement with the sum of ionic radii of 249 pm.[21]

Crystal Structure of $Nd(P_3O_9)\cdot 4.5H_2O$

$Nd(P_3O_9)\cdot 4.5H_2O$ crystallizes in a new structure type adopting the monoclinic space group *C*2/*c*. The neodymium atoms form chains running along [101], with the Nd–Nd distances ranging from 592.6(2) to 594.9(2) pm. In more detail, chains of *trans*-connected Nd_2 pairs with a Nd–Nd distance of 593 pm are formed. Between these *trans*-chains, the cyclotriphosphate anions and crystal water molecules are situated. The Nd^{3+} ions are coordinated by eight oxygen atoms. Five terminal oxygen atoms of a single cyclotriphosphate anion and three oxygen atoms of crystal water molecules form a trigonal prism, bicapped by one crystal water and one terminal oxygen atom (Figure 2). The remaining 1.5 water molecules (OW4 and OW5) per formula unit are present as non-coordinating crystal water. OW4 is apparently so weakly bound, that its content might be versatile and was refined to a 50 % site occupation. Full occupation yielded unrealistically large anharmonic displacement parameters. The Nd–O distances range from 234.1(4) to 257.5(5) pm.

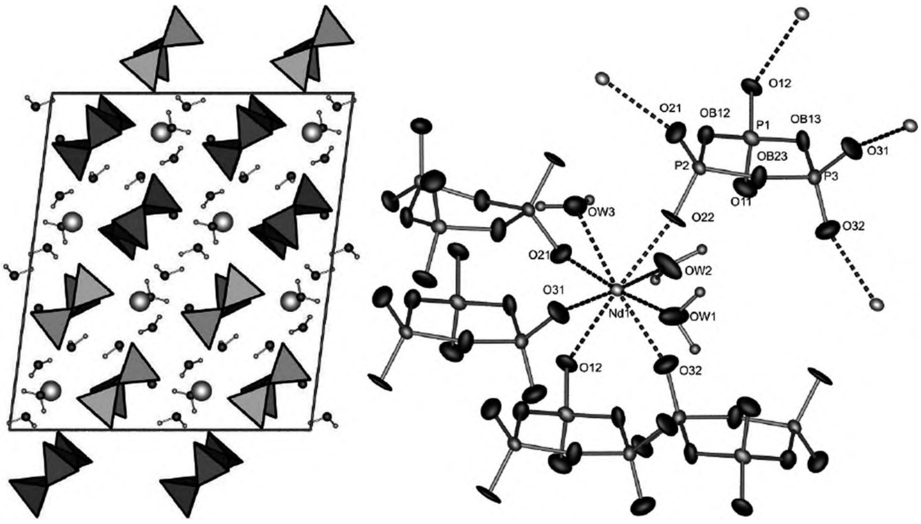

Figure 2. Crystal structure viewed along [010] and coordination of the neodymium atoms in $Nd(P_3O_9)\cdot 4.5H_2O$, the displacement ellipsoids are drawn on a probability level of 50 %.

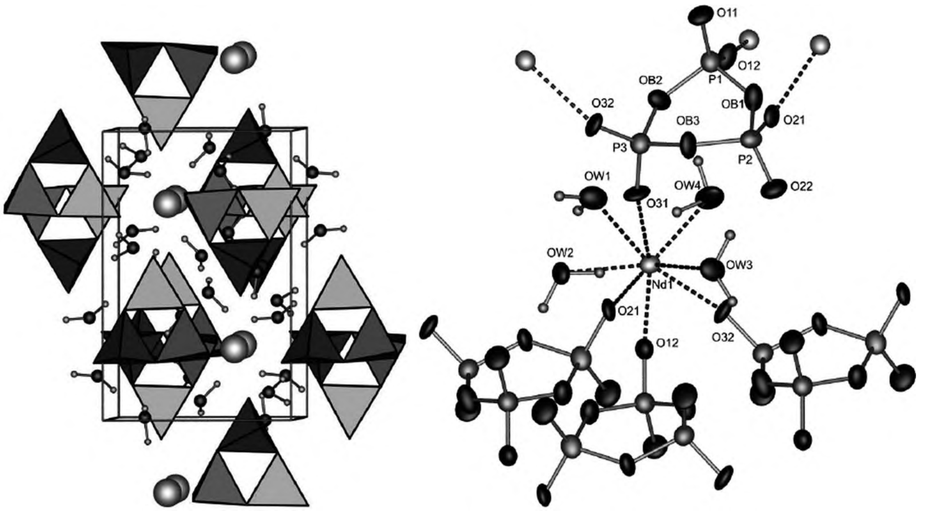

Figure 3. Crystal structure viewed along [001] and coordination of the neodymium atoms in $Nd(P_3O_9)\cdot 5H_2O$, the displacement ellipsoids are drawn on a probability level of 50 %.

Crystal Structure of $Nd(P_3O_9)\cdot 5H_2O$

$Nd(P_3O_9)\cdot 5H_2O$ crystallizes in the monoclinic space group $P2_1/c$. The neodymium atoms form in this new structure type zigzag chains running along [010], with Nd–Nd distances of 666.1(2) pm. Between these chains, the cyclotriphosphate anions and crystal water molecules are positioned. The Nd^{3+} ions are coordinated by eight oxygen atoms with distances ranging between 237.7(8) and 253.9(14) pm. But in contrast to $Nd(P_3O_9)\cdot 4.5H_2O$, only four terminal oxygen atoms of the cyclotriphosphate anion and four oxygen atoms of crystal water molecules contribute to the coordination sphere of the Nd^{3+} cations (Figure 3). The remaining crystal water molecule (OW5) is present as non-coordinating crystal water; its distances to the closest Nd^{3+} ion amount to 463 pm, to the closest crystal water molecules 276 (OW4) and 287 pm (OW1) and the protons form hydrogen bonds to OB3 and O32 (Table S3, Supporting Information) of the cyclotriphosphate anion.

Crystal Structure of $Pr(P_3O_9)\cdot 5H_2O$

$Pr(P_3O_9)\cdot 5H_2O$ adopts a new structure type in the triclinic space group $P\bar{1}$. The praseodymium atoms form zigzag chains running along $[0\bar{1}1]$. The coordination sphere of the Pr^{3+} ions shown in Figure 4 is similar compared with that of $Nd(P_3O_9)\cdot 4.5H_2O$. The coordination polyhedron of the praseodymium atoms can be described as slightly distorted bi-capped trigonal prism. The coordination distances Pr–O lie between 235.3(7) and 255.9(6) pm and are therefore also in good agreement with the sum of the ionic radii of 254 pm.[21]

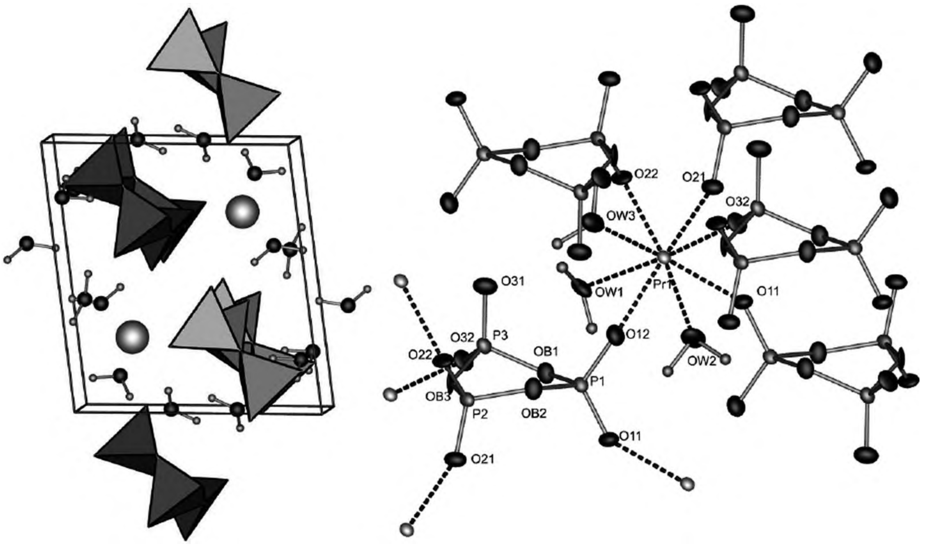

Figure 4. Crystal structure viewed along [100] and coordination of the praseodymium atoms in $Pr(P_3O_9)\cdot 5H_2O$, the displacement ellipsoids are drawn on a probability level of 50 %.

Crystal Structure of $Na_3RE(P_3O_9)_2·6H_2O$ (RE = Pr, Nd)

$Na_3RE(P_3O_9)_2·6H_2O$ (*RE* = Pr, Nd) crystallize in the monoclinic space group $P2_1/n$. In this new structure type, the rare-earth ions are sandwich-type coordinated by two cyclotriphosphate anions. Their coordination sphere is completed by further three crystal water molecules forming a tri-capped trigonal prism (Figure 5) with one of them (OW5) being farther away than the two others. These moieties $[RE(P_3O_9)_2·3H_2O]^{3-}$ form a slightly distorted hexagonal closest packing along [001] (Figure 6). In the voids of this structure the sodium ions and further crystal water molecules are located; an assignment to "octahedral" holes and so forth is not possible. The distances Nd–O range from 242.4(12) to 250.1(11) pm [302(3) pm to OW5], for Pr–O distances between 243.9(7) and 252.1(7) pm [292.8(10) pm towards OW5] are found. Two sodium ions are coordinated fivefold, two sixfold by oxygen (Figure 7) with distances from 222.8(17) to 262.1(10) pm in $Na_3Nd(P_3O_9)_2·6H_2O$ and between 217.9(11) and 259.5(6) pm for $Na_3Pr(P_3O_9)_2·6H_2O$.

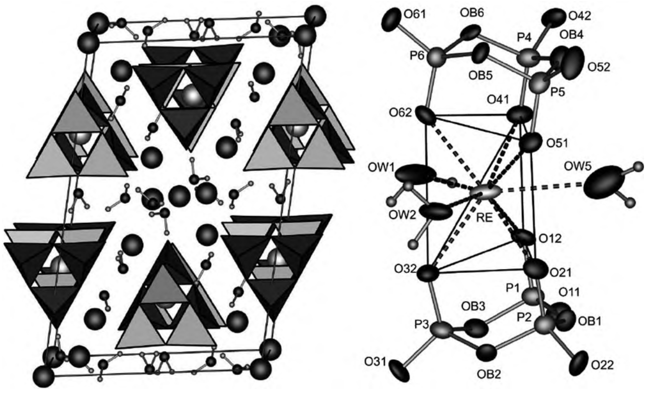

Figure 5. Crystal structure viewed along [010] and coordination of the praseodymium atoms in $Na_3Pr(P_3O_9)_2·6H_2O$, the displacement ellipsoids are drawn on a probability level of 50 %.

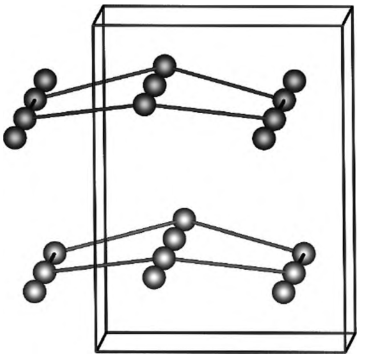

Figure 6. Representation of the distorted *hcp* type arrangement of the *RE* ions in $Na_3RE(P_3O_9)_2·6H_2O$ viewed along [100] ([001] running up); the differently greyed *RE* ions illustrate the two different layers, the lines between them the six-rings typical for densest packed layers.

Discussion of the Structural Data

All title compounds presented in this contribution contain cyclotriphosphate anions, neodymium or praseodymium cations, and crystal water molecules. The bond lengths $P–O^{term}$ ranging from 143.6 to 150.0 pm are shorter than the bond lengths $P–O^{br}$ (156.1–162.4 pm). They agree well with typical bond lengths inside phosphate chains in other *catena*- or cyclophosphates [4,5,22–25]. As observed previously in *catena*- or cyclophosphates, the angles $O^{br}–P–O^{br}$ (99.8° to 103.0°) are significantly smaller compared with the angles $O^{term}–P–O^{term}$ (118.0° to 121.8°). A suited measure for deviations of tetrahedra from the ideal symmetry was suggested by *Balic-Žunic* and *Makovicky*[26,27] and we applied this method already to e.g. polyphosphates such as $Ln(PO_3)_3$ (*Ln* = Sc, Y, Tb – Yb)[21] or phosphate tungstates $NaRE(PO_4)(WO_4)$.[28] For these we identified typical values for condensed phosphate tetrahedra below 1 %. As can be seen from Table 1 all tetrahedra are well below this mark and can thus be regarded as regular.

Table 1. Deviations of the PO_4 tetrahedra from the ideal symmetry after the method of *Balic-Žunic* and *Makovicky*.

Compound	Deviation /%	Compound	Deviation /%
$Nd(P_3O_9)·3H_2O$	0.12	$Pr(P_3O_9)·5H_2O$	0.09–0.20
$Nd(P_3O_9)·4.5H_2O$	0.09–0.23	$Na_3Nd(P_3O_9)_2·6H_2O$	0.12–0.28
$Nd(P_3O_9)·5H_2O$	0.10–0.15	$Na_3Pr(P_3O_9)_2·6H_2O$	0.05–0.22

As expected the average distances between the neodymium ions increase with growing crystal water content from 661 pm [$Nd(P_3O_9)·3H_2O$, 8 distances below 800 pm] via 705 pm [$Nd(P_3O_9)·4.5H_2O$, 7 distances] to 723 pm [$Nd(P_3O_9)·5H_2O$, 7 distances].

The distances of all cations to coordinating oxygen atoms are in very good agreement with the sum of ionic radii and *RE*–O and Na–O distances found in similar oxo salts.

The crystal structures not containing sodium comprise three-dimensional frameworks of rare-earth ions coordinated by cyclotriphosphate ions with the latter ones bonding at least to

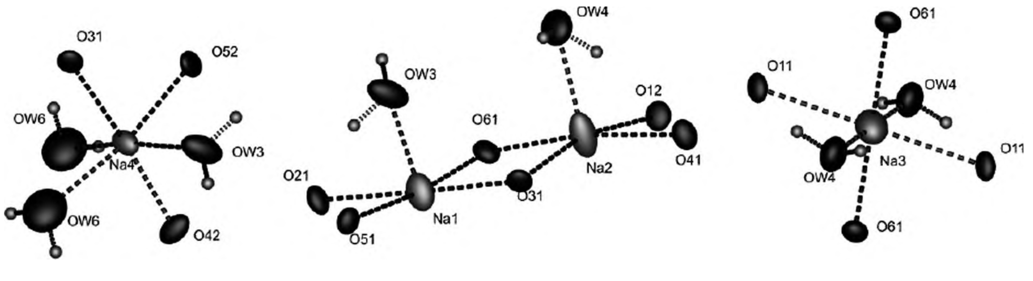

Figure 7. Coordination of the sodium atoms in $Na_3Pr(P_3O_9)_2·6H_2O$, the displacement ellipsoids are drawn on a probability level of 50 %.

four different rare-earth ions [$Nd(P_3O_9)·3H_2O$ six, $Nd(P_3O_9)·4.5H_2O$ five, $Nd(P_3O_9)·5H_2O$ four, $Pr(P_3O_9)·5H_2O$ five]. In contrast, in $Na_3\mathit{RE}(P_3O_9)_2·6H_2O$ (*RE* = Nd, Pr) the complex moieties $[\mathit{RE}(P_3O_9)_2]^{3-}$ form condensed chains along [010] with each cyclotriphosphate connected to only two rare-earth ions. Accordingly, the portion of terminal oxygen atoms of the cyclotriphosphate anions decreases with increasing crystal water content from six [$Nd(P_3O_9)·3H_2O$, CN = 9] via five [$Nd(P_3O_9)·4.5H_2O$, CN = 8] to four [$\mathit{RE}(P_3O_9)·5H_2O$, *RE* = Nd, Pr, CN = 8].

All new compounds of this contribution exhibit extended hydrogen bond networks. Tables S1–S6 (Supporting Information) give an overview about the hydrogen bonds found in the title compounds. The majority of these exhibit distances from donator oxygen *D* atom to its nearest acceptor *A* between 255 and 325 pm and angles $D–H\cdots A$ ranging from 119° to 179° and can therefore be classified as moderate according to hydrogen bond schemes.[29,30] All remaining hydrogen bonds are thus weak as no strong ones could be identified.

Vibrational Spectroscopy of $Nd(P_3O_9)·4.5H_2O$

Figure 8 shows the infrared spectrum of $Nd(P_3O_9)·4.5H_2O$. The infrared spectra of *catena*-polyphosphates are significantly different from those of orthophosphates.[31] The only characteristic bands should be found in the region between 800 and 650 cm^{-1}, where the number of bands should match with the periodicity of the phosphate chain. Here only two bands are resolved in this area. The strongest bands can be assigned to $\nu(PO^{term})$ and $\nu_{as}(PO_2)$ vibrations and range from 1130 to 960 cm^{-1} and from 1360 to 1130 cm^{-1}, respectively. The $\nu_{as}(POP)$ recorded at 920 cm^{-1} is shifted to lower wavenumbers compared with other not strained poly- and oligophosphates, where this band is found around 940 cm^{-1}.[28] Additionally, rather intense H–O vibrations are found with a maximum at 3408 cm^{-1} typical for moderately strong hydrogen bonds.[26,27] The $\delta(H_2O)$ is detected around 1630 cm^{-1}. Finally, intense $\delta(PO_3)$ and $\delta(PO_4)$ are found below 800 cm^{-1}.

Conclusions

In this contribution we shed light on the crystal structures of a series of rare-earth cyclotriphosphate hydrates. With exception of $Nd(P_3O_9)·3H_2O$ all crystal structures represent new structure types. The conformation of the cyclotriphosphate anion does not change during formation from sodium cyclotriphosphate. Only slight changes of crystal water content lead to drastically different structures. Some relevant trends could be identified, though, like the decreasing tendency of the cyclotriphosphate ions to coordinate to the rare-earth cations. Nevertheless, still at the highest crystal water content we observed coordination frameworks instead of isolated hydrated complex moieties as long as no sodium cations were present in the compound. In the latter case indeed "isolated" sandwich complexes $[\mathit{RE}(P_3O_9)_2]^{3-}$ are present.

Since all title compounds exhibit coordinating crystal water molecules, the optical properties of the compounds are of minor interest.

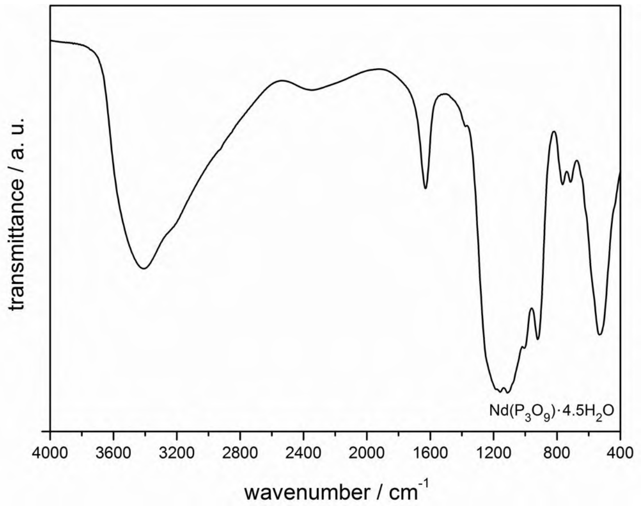

Figure 8. Infrared spectrum of $Nd(P_3O_9)·4.5H_2O$.

The investigations mentioned in the introduction[16,17] as well as many others not given here present powder diffraction patterns of their assumed neodymium cyclotriphosphate hydrates. None of these coincides with one of the new cyclotriphosphate hydrates of our contribution.

Experimental Section

Syntheses: The syntheses were performed according to Equation (1) and Equation (2), starting from aqueous solutions of rare earth chloride and sodium cyclotriphosphate (NaCTP). NaCTP was prepared according to Ref. [32].

$$\mathit{RE}Cl_{3,aq} + Na_3(P_3O_9)_{aq} \rightarrow \mathit{RE}(P_3O_9)·m H_2O_{sol} + 3NaCl_{aq} \quad (1)$$

$$\mathit{RE}Cl_{3,aq} + 2Na_3(P_3O_9)_{aq} \rightarrow Na_3RE(P_3O_9)_2·6H_2O + 3NaCl \quad (2)$$

$Nd(P_3O_9)·4.5H_2O$ and $Pr(P_3O_9)·5H_2O$: A 0.1 molar solution of rare-earth chloride (10 mL) was added to a 0.1 molar solution of NaCTP (10 mL) and left overnight at room temperature. Afterwards the precipitated product was sucked off and washed with little water.

$Nd(P_3O_9)·5H_2O$: The compound was prepared by placing the mother lye from the synthesis of $Nd(P_3O_9)·4.5H_2O$ in a fridge at 0 °C. After a week the created precipitate was sucked off and washed with little amount of cold water.

$Na_3\mathit{RE}(P_3O_9)_2·6H_2O$ (*RE* = Pr, Nd): A 0.1 molar solution of the rare earth chloride (5 mL) was added to a 0.1 molar solution of NaCTP (5 mL) and left at room temperature until the water was evaporated.

$Nd(P_3O_9)·3H_2O$: In contrast to the other compounds, $Nd(P_3O_9)·3H_2O$ was prepared in a solid-state reaction by transferring a mixture of $NdCl_3·6H_2O$ (128.7 mg, Ventron, 99.9 %) and P_4O_{10} (105.2 mg, Aldrich, 98 %) to a alumina boat and heating to 120 °C with a rate of $30°·h^{-1}$; the mixture was maintained at this temperature for 60 h and finally slowly cooled to room temperature ($5\ °C·h^{-1}$).

Crystal Structure Analyses: Suitable single-crystals of all title compounds were selected under a polarising microscope and enclosed in glass capillaries. X-ray diffraction data were collected with a Stoe IPDS II area detection diffractometer and corrected numerically for

Table 2. Crystallographic data (estimated standard deviations in parentheses).

	$Nd(P_3O_9)\cdot 3H_2O$	$Nd(P_3O_9)\cdot 4.5H_2O$	$Nd(P_3O_9)\cdot 5H_2O$	$Pr(P_3O_9)\cdot 5H_2O$	$Na_3Nd(P_3O_9)_2\cdot 6H_2O$	$Na_3Pr(P_3O_9)_2\cdot 6H_2O$
Temperature /K	293(2)					
Crystal system	hexagonal	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{6}$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a /pm	677.90(9)	1644.6(3)	773.75(15)	745.64(15)	1059.78(18)	1061.42(16)
b /pm		756.11(15)	1149.1(2)	889.07(18)	1207.25(15)	1209.0(2)
c /pm	608.67(9)	1856.1(4)	1394.9(3)	934.55(19)	1645.7(4)	1635.5(3)
α /°				79.00(3)		
β /°		97.25(3)	106.07(3)	80.25(3)	99.742(17)	99.841(13)
γ /°				66.48(3)		
V /$10^6\cdot pm^3$	242.24(6)	2289.5(8)	1191.8(4)	554.64(19)	2075.2(7)	2067.9(6)
Z	3	8	4	2	4	4
Calculated density D_x /$g\cdot cm^{-3}$	2.983	2.682	2.626	2.802	2.545	2.543
$\mu(Mo\text{-}K_\alpha)$ /mm^{-1}	5.913	5.023	4.830	4.901	3.141	2.997
Radiation	Mo-K_α radiation					
Diffractometer	STOE IPDS 2					
Absorption correction	numerical					
Index range	$-8 < h < 8$	$-19 < h < 19$	$-8 < h < 9$	$-8 < h < 8$	$-10 < h < 10$	$-11 < h < 11$
	$-8 < k < 8$	$-8 < k < 8$	$-13 < k < 13$	$-10 < k < 10$	$-11 < k < 11$	$-13 < k < 12$
	$-7 < l < 7$	$0 < l < 22$	$-15 < l < 16$	$-11 < l < 11$	$0 < l < 15$	$-17 < l < 17$
Theta range ($\theta_{min}-\theta_{max}$)	3.35–24.96	2.21–25.00	1.52–24.96	2.23–24.99	2.10–19.99	2.11–22.50
Reflections collected	313	2006	2106	1842	1924	2704
Independent reflections	312	1763	1338	1468	1109	1323
Parameters	36	194	194	193	351	350
R_{int} / R_{sigma}	0.045 /0.025	0.038 / 0.037	0.081 / 0.122	0.059 / 0.084	0.116 / 0.153	0.097 / 0.158
R values	$R_1 = 0.016$	$R_1 = 0.032$	$R_1 = 0.042$	$R_1 = 0.036$	$R_1 = 0.047$	$R_1 = 0.035$
	$wR_2 = 0.038$	$wR_2 = 0.081$	$wR_2 = 0.082$	$wR_2 = 0.089$	$wR_2 = 0.119$	$wR_2 = 0.062$
R_1(all data)	$R_1 = 0.016$	$R_1 = 0.037$	$R_1 = 0.079$	$R_1 = 0.052$	$R_1 = 0.085$	$R_1 = 0.108$
Goodness of fit (GooF)	1.128	1.024	0.821	0.982	0.830	0.657
Residual electron density, min/max	–0.492 / 0.378	–1.252 / 1.868	–0.940 / 1.782	–0.947 / 1.330	–0.756 / 1.035	–0.765 / 0.450
Comments			twin: BASF: 0.37042			

Table 3. Selected interatomic distances /pm and angles /° of cyclotriphosphate hydrates in this contribution (estimated standard deviations in parentheses).

Distances / angles	$Nd(P_3O_9)\cdot 3H_2O$	$Nd(P_3O_9)\cdot 4.5H_2O$	$Nd(P_3O_9)\cdot 5H_2O$	$Pr(P_3O_9)\cdot 5H_2O$	$Na_3Nd(P_3O_9)_2\cdot 6H_2O$	$Na_3Nd(P_3O_9)_2\cdot 6H_2O$
RE–O	251.5(3), 258.7(5)	234.1(4)–257.5(5)	237.7(8)–253.9(14)	235.3(7)–255.9(6)	242.4(12)–250.1(11), 302(3)	2.439(7)–2.521(7), 2.928(10)
Na–O					222.8(17)–262.1(10)	2.179(11)–2.595(6)
$P–O^{term}$	147.0(3)	145.2(5)–147.7(5)	143.8(11)–147.9(9)	143.6(7)–145.1(7)	145.2(11)–149.7(13)	1.459(7)–1.500(7)
$P–O^{br}$	158.5(5)	158.3(4)–160.1(4)	156.7(11)–162.3(10)	156.1(7)–159.1(8)	158.7(13)–162.4(12)	1.597(7)–1.623(7)
$O^{term}–P–O^{term}$	119.4(4)	118.8(3)–120.3(3)	118.0(6)–120.5(6)	118.6(4)–119.5(4)	118.0(8)–121.6(7)	119.5(4)–121.8(4)
$O^{br}–P–O^{term}$	107.3(2), 109.3(2)	106.4(3)–110.3(3)	106.7(6)–110.4(7)	106.2(4)–111.0(5)	106.8(6)–111.2(7)	107.0(4)–110.9(4)
$O^{br}–P–O^{br}$	103.0(3)	100.8(2)–102.9(2)	100.9(5)–101.7(5)	100.9(4)–102.4(4)	99.8(6)–101.5(6)	100.0(4)–101.1(4)

absorption.[33] The crystal structures were solved by direct methods and refined by least square refinements using SHELXTL.[34] In all cases refinements were performed with anisotropic displacement parameters for all non hydrogen atoms.

In the case of $Nd(P_3O_9)\cdot 5H_2O$ the crystal structure was solved and refined in space group $P2_1/c$. Initially it was only possible to localize the neodymium atoms and the cyclotriphosphate anion with very large ADPs. The close relationship to an orthorhombic *C*-centered cell with the lattice parameters a = 773.8, b = 2680.8 and c = 1149.1 pm via the matrix (–100 / 102 / 010) revealed the presence of a pseudo-merohedral twin obeying the twin law (–100 / 0–10 / 101); now all atoms could be located and refined with acceptable residuals.

The relevant crystallographic data and further details of the X-ray data collection are summarized in Table 2. In Table 3 selected interatomic distances and angles are listed.

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD-426743 [for $Nd(P_3O_9)\cdot 3H_2O$], CSD-426744 [for $Nd(P_3O_9)\cdot 4.5H_2O$], CSD-426746 [for $Pr(P_3O_9)\cdot 5H_2O$], CSD-426745 [for $Nd(P_3O_9)\cdot 5H_2O$], CSD-426748 [for $Na_3Nd(P_3O_9)_2\cdot 6H_2O$], and CSD-426747 [for $Na_3Pr(P_3O_9)_2\cdot 6H_2O$].

Infrared Spectroscopy: An FTIR spectrum was obtained at room temperature with a Bruker IFS 66v/S spectrometer. The samples were thoroughly mixed with dried KBr (approx. 2 mg sample, 300 mg KBr).

Supporting Information (see footnote on the first page of this article): Tables with details of the hydrogen bond networks identified in the title compounds.

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