Journal of Alloys and Compounds, 176 (1991) 337–345
JAL 0065

$Pr_2(OH)_3H_2O(ClO_4)_3$, a new example of an inner-sphere lanthanide perchlorate complex

Thomas Schleid and Gerd Meyer
Institut für Anorganische Chemie, Universität Hannover, Callinstrasse 9, W-3000 Hannover 1 (F.R.G.)

Grażyna Oczko and Janina Legendziewicz
Institute of Chemistry, University of Wrocław, 14 Joliot-Curie Street, PL-50-383 Wrocław (Poland)

(Received June 9, 1991)

Abstract

The crystal structure of Pr(III) hydroxide perchlorate monohydrate, $Pr_2(OH)_3H_2O(ClO_4)_3$, has been determined from single-crystal X-ray diffraction data. The unit cell (monoclinic, $C2/c$, $a = 1576.1(4)$ pm, $b = 961.8(3)$ pm, $c = 1033.2(3)$ pm, $\beta = 119.97(3)$°, $Z = 4$, $R = 0.023$, $R_w = 0.022$) contains eight Pr^{3+} ions in ninefold oxygen coordination. Seven O^{2-} ions from perchlorate anions and two O^{2-} ions from hydroxide anions or crystal water form a distorted tricapped trigonal prism surrounding Pr^{3+}. Two crystallographically and functionally different ClO_4^- anions bridge two Pr^{3+} cations to form anionic centrosymmetric dimers with the composition $\{[Pr(OH)_{3/2}(H_2O)_{1/2}(ClO_4)_4]_2\}^{5-}$. Further connection via "free" coordination positions of perchlorate oxygen leads to one-dimensional infinite chains which run parallel to [001]. These are stacked in the [010] direction in the fashion of a hexagonal closest packing of rods that are further connected via perchlorate oxygen assisted by (weak) hydrogen bonds to form a three-dimensional network.

1. Introduction

For a long time, it was assumed that perchlorate anions (ClO_4^-) have only little tendency to form inner-sphere complexes with the lanthanides in aqueous solutions [1–6]. Recently, however, X-ray single-crystal structure determinations on $Pr_2(L\text{-}Glu)_2(ClO_4)_4 \cdot 11H_2O$ [7] and $Nd_2(OH)_3(ClO_4)_3 \cdot 5H_2O$ [8, 9] were reported, both with ClO_4^- as an inner-sphere ligand of the trivalent lanthanide cation. Since both compounds may be obtained from aqueous solutions, there is strong evidence that perchlorate can really compete with H_2O molecules for an inner-sphere coordination position at the lanthanide cation.

Here we present X-ray single-crystal data for the praseodymium hydroxide perchlorate monohydrate, $Pr_2(OH)_3(ClO_4)_3 \cdot H_2O$, as a new example for an inner-sphere lanthanide perchlorate complex compound. Although it is only a (by four H_2O molecules poorer) homologue to $Nd_2(OH)_3(ClO_4)_3 \cdot 5H_2O$, the structural features are completely different.

0925-8388/91/$3.50

2. Experimental details

Single crystals of $Pr_2(OH)_3(ClO_4)_3 \cdot H_2O$ are formed in minor quantities as a cocrystallization product when Pr_6O_{11} (99.99%, Pierce Inorganics) is dissolved in an aqueous solution of trichloroacetic acid (99.9%, Fluka) in order to prepare $Pr(Cl_3CCOO)_3 \cdot 2H_2O$ [10] (molar ratio Pr^{3+}:Cl_3CCOO^- = 1:3, pH ≈ 5.4, maintained by a small amount of free $HClO_4$). Under these conditions the trichloroacetate (pale green, soft, lath shaped, often severely twinned crystals of $Pr(Cl_3CCOO)_3 \cdot 2H_2O$) is the main product. Even with higher ClO_4^- concentrations and varying pH values, $Pr_2(OH)_3H_2O(ClO_4)_3$ was never obtained as a pure product under otherwise similar conditions.

Pale green coarse single crystals of the title compound were selected under sodium-dried mineral oil from the product of such a cocrystallization experiment. Since they are of only limited stability in moist air, they were sealed into thin-walled glass capillaries and their quality was checked by X-ray film techniques. Intensity data of the best specimen selected were recorded with an automatic four-circle diffractometer. Table 1 summarizes the details of the data collection and the determination and refinement of the crystal structure.

3. Results

According to structure determination and refinement (Table 1), the investigated single crystal turned out to be of a basic perchlorate monohydrate of praseodymium with the composition $Pr_2(OH)_3H_2O(ClO_4)_3$. The crystal structure (monoclinic, space group $C2/c$ (number 15), $a = 1576.1(4)$ pm, $b = 961.8(3)$ pm, $c = 1033.2(3)$ pm, $\beta = 119.97(3)°$, $Z = 4$, $R = 0.023$, $R_w = 0.022$) contains eight Pr^{3+} in ninefold oxygen coordination. Seven O^{2-} from perchlorate anions and two O^{2-} from hydroxide anions (or coordinating crystal water) form a slightly distorted tricapped trigonal prism around each Pr^{3+} (Fig. 1; for important distances see Table 2). Two crystallographically and functionally different perchlorate anions, $(O_4Cl1)^-$ and $(O_4Cl2)^-$ in a 2:1 ratio, bridge two Pr^{3+} cations to form anionic centrosymmetric dimers of the composition $\{[Pr(O3H)\{(O4H)_{1/2}(O4H_2)_{1/2}\}(O_4Cl1)_3(O_4Cl2)]_2\}^{5-}$ (see Fig. 2). Thereby $(O_4Cl2)^-$ functions as a "tridentate-bridging" [14] ligand in the way that the bridge (Pr–O21–Cl2–O22–Pr′) is assisted by an O21′–Pr interaction ($d = 278.1$ pm, see Table 2) completing the $(O_4Cl2)^-$ function to become a chelatizing (O21–Cl2–O22) unit for every Pr^{3+} as well. The three $(O_4Cl1)^-$ groups per Pr^{3+} have different functions in the dimer: one $(O_4Cl1)^-$ serves as a "Z,Z-bidentate-bridging" [14] ligand via Pr–O12–Cl1–O14–Pr′; the two remaining $(O_4Cl1)^-$ are just terminal via O11 and O13 to each Pr^{3+} of the dimer (see Fig. 2). The Pr^{3+}–Pr^{3+} distance within the dimer is rather short (430.4 pm) compared with all other Pr^{3+}–Pr^{3+} separations in this compound. Hydroxide (OH^-) and crystal water (H_2O) are represented by O3w and O4w. Note that centrosymmetry and the composition

TABLE 1

$Pr_2(OH)_3(ClO_4)_3 \cdot H_2O$: crystallographic data and their determination

		Atom positions		
		x/a	y/b	z/c
Pr	(8f)	0.11955(2)	0.14332(3)	0.56624(3)
O11	(8f)	0.1333(3)	0.2382(4)	0.3606(4)
O12	(8f)	0.1649(3)	0.9331(4)	0.7195(4)
O13	(8f)	0.2840(3)	0.1978(4)	0.7732(4)
O14	(8f)	0.0445(3)	0.7504(4)	0.5944(4)
Cl1	(8f)	0.13901(8)	0.7867(1)	0.7245(1)
O21	(8f)	0.0244(3)	0.0338(4)	0.8826(4)
O22	(8f)	0.0863(3)	0.2072(4)	0.7756(4)
Cl2	(4e)	0	0.1220(2)	0.75
O3w	(8f)	0.1242(3)	0.4050(4)	0.5931(4)
O4w	(8f)	0.2454(3)	0.0136(4)	0.0435(4)

Displacement coefficients[a]

U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
90(1)	122(1)	95(1)	1(1)	33(1)	−3(1)
269(20)	228(18)	213(20)	3(15)	154(17)	2(15)
173(18)	221(18)	221(19)	42(15)	82(16)	−4(15)
143(17)	258(18)	218(20)	40(15)	75(16)	−42(14)
139(18)	233(18)	214(19)	5(15)	43(16)	35(14)
136(5)	170(5)	140(6)	14(4)	57(5)	14(4)
142(17)	202(17)	129(17)	54(14)	47(14)	11(13)
251(20)	249(18)	238(20)	−46(16)	153(17)	−73(16)
151(8)	151(7)	149(8)	0	75(7)	0
235(20)	236(19)	292(23)	−34(16)	87(18)	−16(16)
239(21)	310(20)	255(21)	−40(17)	129(18)	−24(16)

Four-circle diffractometer data: $a = 1576.1(4)$ pm; $b = 961.8(3)$ pm; $c = 1033.2(3)$ pm; $\beta = 119.97(3)°$; $V_m = 204.27(6)$ cm^3 mol^{-1}.

Crystal system: monoclinic; space group $C2/c$ (number15); $Z = 4$.

Data collection: four-circle diffractometer Siemens-Stoe AED 2, Mo $K\alpha$ radiation; graphite monochromator, $\lambda = 71.07$ pm, ω scan; scan width and speed, variable ("learnt-profile" method [11]); $2° \leqslant \theta \leqslant 26°$, $F(000) = 1188$, $\mu = 77.55$ cm^{-1}.

Data corrections: background, polarization and Lorentz factors; absorption, Ψ scan ($\Delta \Psi = 10°$) for 20 reflections.

Data statistics: 2975 reflections measured of which 1400 were symmetrically independent ($R_{int} = 0.043$), 1377 with $|F_o| \geqslant 2\sigma(F_o)$.

Structure determination and refinement: program SHELX-76 [12], scattering factors from Cromer and Mann [13], Patterson (Pr) and successive difference Fourier syntheses (Cl and O); "full-matrix least-squares" refinement; $R = 0.023$, $R_w = 0.022$ ($w = k[\sigma(F_o)]^{-2}$, $k = 3.523$).

[a] Coefficients of the "anisotropic" thermal displacement factors: $\exp[-2\pi^2 (a^{*2}h^2U_{11} + \ldots + b^*c^*kl_2U_{23} + \ldots)]$, U_{ij} (pm^2).

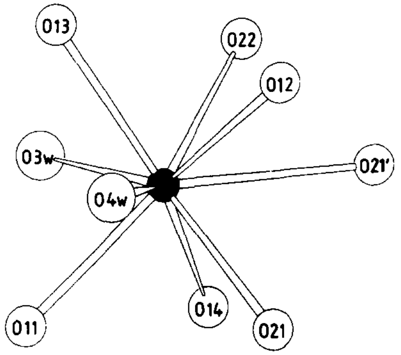

Fig. 1. Polyhedron of coordination of nine oxygen atoms around Pr^{3+} in $Pr_2(OH)_3H_2O(ClO_4)_3$.

TABLE 2

Important internuclear distances (pm) in $Pr_2(OH)_3(ClO_4)_3 \cdot H_2O$ and $Nd_2(OH)_3(ClO_4)_3 \cdot 5H_2O$

Bond	Distance (pm)	Bond	Distance (pm)
Pr–O11	242.0	Nd–O22	237.3
Pr–O21	243.1	Nd–O12	238.5
Pr–O12	244.5	Nd–O2w	240.4
Pr–O13	245.5	Nd–O13	243.1
Pr–O14	248.9	Nd–O4w	245.0
Pr–O3w	252.9	Nd–O11	250.7
Pr–O22	254.2	Nd–O1w	251.1
Pr–O4w	259.5	Nd–O3w	255.0
Pr–O21'	278.1	$(Nd–O)_{av}$	245.1[a]
$(Pr–O)_{av}$	248.8[a] 252.1[b]		
Cl1–O14	146.5	Cl1–O14	145.2
Cl1–O11	147.3	Cl1–O12	146.2
Cl1–O12	147.4	Cl1–O13	146.9
Cl1–O13	147.5	Cl1–O11	150.2
$(Cl1–O)_{av}$	147.2[c]	$(Cl1–O)_{av}$	147.1[c]
Cl2–O21	148.9[d]	Cl2–O21	147.0[d]
Cl2–O22	149.4[d]	Cl2–O22	147.2[d]
$(Cl2–O)_{av}$	149.2[c]	$(Cl2–O)_{av}$	147.1[c]

[a] CN8.
[b] CN9.
[c] CN4.
[d] 2×.

$\{[Pr(O3H)\{(O4H)_{1/2}(O4H_2)_{1/2}\}(ClO_4)_4]_2\}^{5-}$ of the dimers are only possible when one Ow (most probably O3w) represents OH$^-$, while the other one (O4w) has to be both OH$^-$ and H_2O in a 1:1 ratio.

Further connection via free coordination positions (oxygen) of the perchlorate anions leads to one-dimensional infinite chains which run parallel to [001] (Fig. 3). Here $(O_4Cl2)^-$ is used as a "tridentate-bridging" ligand

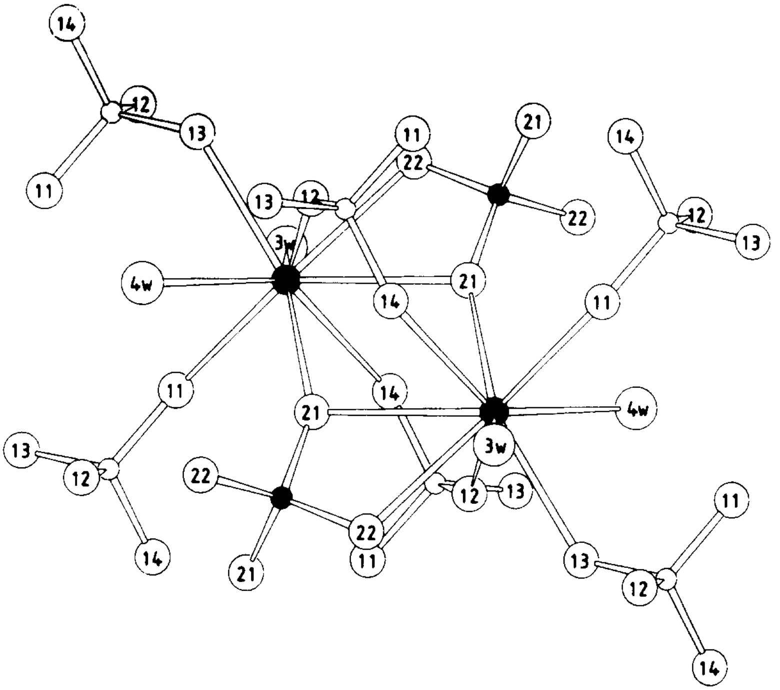

Fig. 2. Centrosymmetric anionic dimer with the composition $\{[\mathrm{Pr(O3H)\{(O4H)_{1/2}(O4H_2)_{1/2}\}}$-$\mathrm{(O_4Cl1)_3(O_4Cl2)}]_2\}^{5-}$ in $\mathrm{Pr_2(OH)_3H_2O(ClO_4)_3}$: ●, Pr (large), Cl2 (small); ○, Ow (large), O (medium), Cl1 (small).

again so that $(\mathrm{O_4Cl2})^-$ *in summa* becomes a hexadentate ligand. Simultaneously, $(\mathrm{O_4Cl2})^-$ serves as a "Z,Z-bidentate-bridging" ligand in the chain direction, here as a Pr–O21–Cl2–O21–Pr, a Pr–O21–Cl2–O22–Pr, a Pr–O22–Cl2–O21–Pr and a Pr–O22–Cl2–O22–Pr clamp with Pr–Pr distances of 568.3 pm and 585.6 pm respectively (Fig. 3). The three $(\mathrm{O_4Cl1})^-$ per $\mathrm{Pr^{3+}}$ again act differently for the interconnection of the dimers to a chain: the (so far) "Z,Z-bidentate-bridging" Pr–O12–Cl1–O14–Pr perchlorate uses O11 as a terminal ligand for two other dimers, so that another "Z,Z-bidentate-bridging" function Pr–O14–Cl1–O11–Pr forms as an "intrachain connector". On the other hand, this also works *vice versa*: the (so far) O11-terminal $(\mathrm{O_4Cl1})^-$ groups of one dimer function as "Z,Z-bidentate-bridging" Pr–O12–Cl1–O14–Pr clamps for two other dimers. This involves O11, O12 and O14 from $(\mathrm{O_4Cl1})^-$ perchlorate in bonds to $\mathrm{Pr^{3+}}$ along the [001] chain direction (see Fig. 3).

The arrows depicting O13 in $(\mathrm{O_4Cl1})^-$ in Fig. 3 indicate that these are the only "free" coordinating positions of any perchlorate anion left over. Since the chains spread out along [001] and are stacked in the [010] direction like a hexagonal closest packing of rods, even the O13 atoms become coordinating. They are, finally, connecting the chains to form a rather complicated three-dimensional network (Fig. 4), assisted by hydrogen bonds from O3w and O4w to perchlorate oxygen. Thereby three new "Z,Z-bidentate-

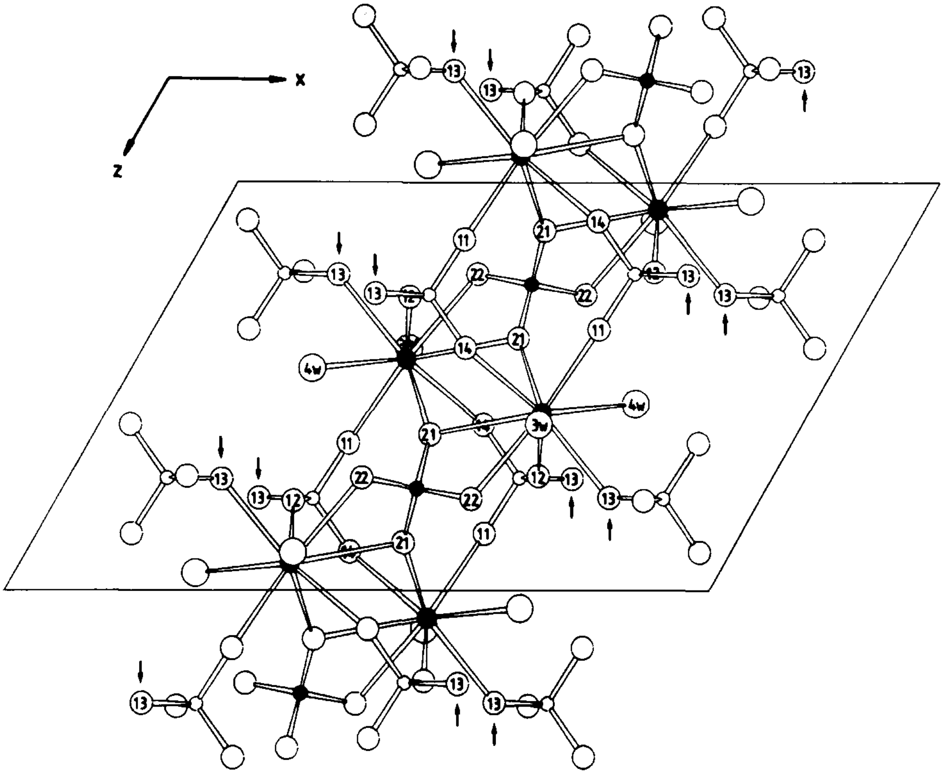

Fig. 3. One-dimensional infinite chain built up from centrosymmetric dimers (see Fig. 2). O13 atoms are depicted by arrows for clarification of Fig. 4.

bridging" functions (Pr^{ic}–O11–Cl1–O13–Pr^{nc}, Pr^{ic}–O12–Cl1–O13–Pr^{nc} and Pr^{ic}–O14–Cl1–O13–Pr^{nc}; ic denotes *ipso* chain, nc denotes neighbouring chain) of $(O_4Cl1)^-$ as "cross-linkers" of the chains are generated as well. It is remarkable that all shortest Pr–Pr interchain distances from *ipso* to neighbouring chains are with 534.9 pm somewhat shorter than the intrachain distances (568.3 and 585.6 pm) coupling the dimers (with $d(\text{Pr–Pr}') = 430.4$ pm). Hydrogen bond assistance for the connection of the chains is hard to prove since hydrogen positions were impossible to detect or to refine. Although the investigated crystal was of high quality (see Table 1) the residual electron density after the final refinement cycles was only at a value of 0.9 e^- $Å^{-3}$ or less in $x/a = 0.136$, $y/b = 0.056$ and $z/c = 0.587$ (*i.e.* 88 pm from praseodymium), but there was no evidence for hydrogen close to O3w and O4w in the final difference Fourier map. Hydrogen bonding in the system under consideration can therefore only be concluded from "short" O–O distances ($d(\text{O}n\text{w–O1}n) \leq 300$ pm, namely 281 pm (O3w–O14), 291 pm (O3w–O12), 295 pm (O3w–O11), 274 pm (O4w–O12) and 295 pm (O4w–O13)) between O3w, O4w and perchlorate oxygen atoms of the $(O_4Cl1)^-$ anion. $(O_4Cl2)^-$ can hardly be involved in the hydrogen bond system judging from distances such as 294 pm (O3w–O22) and 303 pm (O4w–O21).

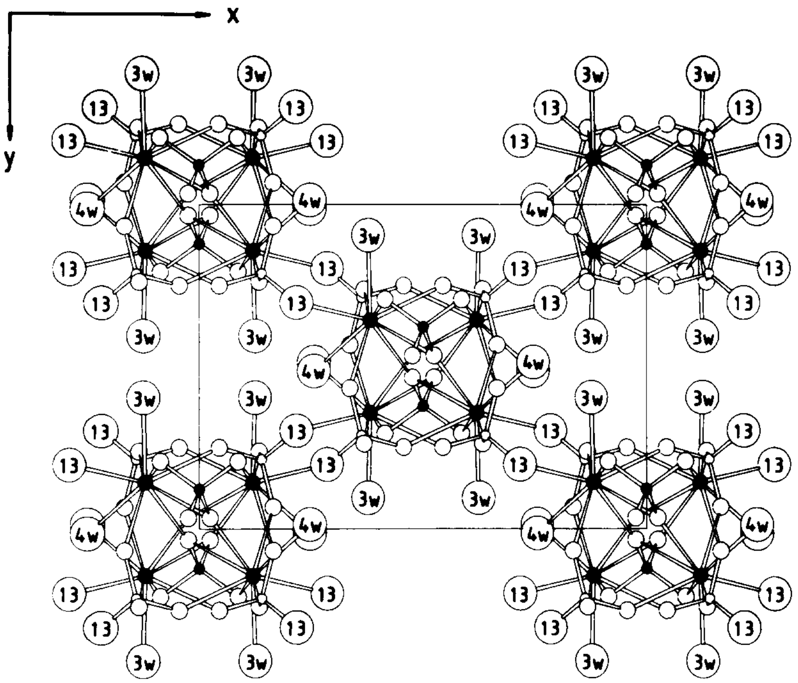

Fig. 4. Arrangement of the chains (see Fig. 3) in the fashion of a hexagonal closest packing of rods and their interconnection via O13 oxygen atoms (assisted by hydrogen bonding from O3w and O4w).

4. Discussion

The crystal structure of $Pr_2(OH)_3H_2O(ClO_4)_3$ shows some remarkable differences from that of $Nd_2(OH)_3(H_2O)_5(ClO_4)_3$ [8] although it is formally just a (by four crystal water molecules poorer) homologue. The neodymium compound contains Nd^{3+} in an eightfold oxygen coordination; Pr^{3+} in $Pr_2(OH)_3H_2O(ClO_4)_3$ has a coordination number of nine (better: eight plus one because the ninth ligand (O21′) is by 12% further apart than the mean distance to the eight other oxygen atoms). Nd^{3+} has four H_2O or OH^- ligands (two of them are crystal water, one of them is OH^-, and the remainder is both OH^- and H_2O in a 1:1 ratio) and four oxygen ligands from perchlorate anions. Pr^{3+}, however, has just two OH^- or H_2O ligands (one of them is OH^-, the other one both OH^- and H_2O in a 1:1 ratio) and seven oxygen ligands from perchlorate anions. Both compounds contain two crystallographically and functionally different perchlorate groups, $(O_4Cl1)^-$ and $(O_4Cl2)^-$, with a 2:1 multiplicity. In the neodymium compound, $(O_4Cl2)^-$ works as a "Z,Z-bidentate-bridging" ligand exclusively, with only two O22 as coordinative perchlorate oxygen atoms while the two O21 do not belong to Nd^{3+}. $(O_4Cl1)^-$ has three of its oxygen atoms (O11, O12 and O13) coordinating Nd^{3+} while only O14 remains free. The function of $(O_4Cl1)^-$ is three times "Z,Z-bidentate-bridging" in forming Nd–O11–Cl1–O12–Nd, Nd–O11–Cl1–O13–Nd and Nd–O12–Cl1–O13–Nd clamps simultaneously. By this kind of connection, a (two-dimensional) puckered layer structure of Nd^{3+} with ClO_4^- is built up, providing a rather homogeneous Nd^{3+}–Nd^{3+} distance spectrum (513 and 556 pm). Interconnection and charge compensation of these (cationic) layers is achieved by water molecules and/or hydroxide anions assisted by (weak) hydrogen bonds. For further details with respect to important distances see Table 2 and ref.8.

$Pr_2(OH)_3H_2O(ClO_4)_3$ has to be more highly condensed (with four molecules of H_2O less) and this is exactly what crystal structure and density ($D_x = 3.18$ g cm^{-3} *vs.* 2.88 g cm^{-3} for $Nd_2(OH)_3(H_2O)_5(ClO_4)_3$) show. However, the association of H_2O or OH^- with certain Ow oxygen atoms remains puzzling. As shown in ref. 8 where hydrogen positions for $Nd_2(OH)_3(ClO_4)_3 \cdot 5H_2O$ were determined and refined, the shortest bond Nd–Ow (*i.e.* 240 pm for Nd–O2w; $O2w \equiv H_2O$) is not an Nd^{3+}–OH^- contact as one might assume. Moreover, the longest separation (Nd–O3w: 255 pm) belongs to O3w which is both H_2O and OH^-, while 245 pm (Nd–O4w; $O4w \equiv OH^-$) and 251 pm (Nd–O1w; $O1w \equiv H_2O$) are distances within the expectations. Therefore the necessary distribution of OH^- and H_2O over the available O3w and O4w sites as given above for $Pr_2(OH)_3(ClO_4)_3 \cdot H_2O$ (where no hydrogen positions could have been determined) just by means of bond lengths and charge arguments is rather hazardous.

Mean Cl–O distances of 147 pm and angles between 107° and 112° were observed for both perchlorate anions in the neodymium compound. In the praseodymium compound, a mean distance of 147 pm is found for $(O_4Cl1)^-$ as well whereas $(O_4Cl2)^-$ shows longer Cl–O contacts (mean, 149 pm), obviously due to the higher number (six) of O–Nd coordinations. This also affects the angles: while $(O_4Cl1)^-$ (109°–112°) behaves "normally", $(O_4Cl2)^-$ exhibits angles between 105° and 114° deviating somewhat more from the tetrahedral angle of 109.5°. It is worth mentioning that the "tridentate-bridging" character of perchlorate, namely $(O_4Cl2)^-$ in the title compound, is found for the first time ever in ClO_4^- coordination chemistry [15]. Frequently, it occurs in lanthanide carboxylates [14, 16, 17], while perchlorates in inner-sphere coordination usually function in a mono- or bidentate ("Z,Z-bridging") manner [18, 19], as $(O_4Cl1)^-$ does in $Pr_2(OH)_3(ClO_4)_3 \cdot H_2O$.

Finally, calculations on the basis of Biltz's volume increments $V_{m,i}$ [20] reveal that the difference in molar volume ($V_m = 252.8$ cm^3 mol^{-1} for $Nd_2(OH)_3(ClO_4)_3 \cdot 5H_2O$ *vs.* 204.3 cm^3 mol^{-1} for $Pr_2(OH)_3(ClO_4)_3 \cdot H_2O$, $\Delta V_m = 48.5$ cm^3 mol^{-1}) corresponds reasonably well with a residual volume that four water molecules ($V_{m,i}(H_2O) \approx 12$ cm^3 mol^{-1} [20]) require. Both compounds can be built up properly when volume increments of 11–12 cm^3 mol^{-1} for H_2O (or OH^-) and 50–52 cm^3 mol^{-1} for ClO_4^- are used and the molar volume of the trivalent lanthanide cation is neglected.

Acknowledgment

This work has been supported by the Fonds der Chemischen Industrie, Frankfurt-am-Main, F.R.G.

References

1 F. H. Spedding, L. E. Shiers and J. A. Rard, *J. Chem. Eng. Data*, *20* (1975) 66.
F. H. Spedding, M. A. Mohs, J. L. Derer and A. Habenschuss, *J. Chem. Eng. Data*, *22* (1977) 142.
2 J. Glaser and G. Johansson, *Acta Chem. Scand. A*, *35* (1981) 639.
G. Johansson, L. Niinistö and H. Wakita, *Acta Chem. Scand. A*, *39* (1985) 359.
3 G. Johansson and H. Yokoyama, *Inorg. Chem.*, *29* (1990) 2460.
4 P. J. Breen and W. de W. Horrocks, Jr., *Inorg. Chem.*, *22* (1983) 536.
F. Tanaka and S. Yamashita, *Inorg. Chem.*, *23* (1984) 2044.
5 E. Brücher, J. Glaser, I. Grenthe and I. Puigdomenech, *Inorg. Chim. Acta*, *109* (1985) 111.
C. Cossy and A. E. Merbach, *Pure Appl. Chem.*, *60* (1988) 1785.
6 L. Niinistö and M. Leskelä, in K. A. Gschneidner, Jr., and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 9, Elsevier, Amsterdam, 1987, p. 91.
7 I. Csöregh, P. Kierkegaard, J. Legendziewicz and E. Huskowska, *Acta Chem. Scand. A*, *41* (1987) 453.
8 I. Csöregh, E. Huskowska, A. Ertan, J. Legendziewicz and P. Kierkegaard, *Acta Chem. Scand. A*, *43* (1989) 829.
9 E. Huskowska, J. Legendziewicz and J. Hanuza, *Polyhedron*, *9* (1990) 659.
10 J. Legendziewicz, C. Szafranski, G. Oczko, W. Strek and B. Jezowska-Trzebiatowska, *Bull. Acad. Polon. Sci.*, *Cl. 3*, *36* (1988) 189.
11 W. Clegg, *Acta Crystallogr. A*, *37* (1981) 22.
12 G. M. Sheldrick, *SHELX-76 program for the determination of crystal structures from X-ray diffractometer data*, Cambridge, 1976.
13 D. T. Cromer and J. B. Mann, *Acta Crystallogr. A*, *24* (1968) 321.
D. T. Cromer and D. Liberman, *J. Chem. Phys.*, *53* (1970) 1891.
14 A. Ouchi, Y. Suzuki, Y. Ohki and Y. Koizumi, *Coord. Chem. Rev.*, *92* (1988) 29.
15 C. Belin, M. Chaabouni, J. L. Pascal and J. Potier, *Inorg. Chem.*, *21* (1982) 3557.
J. L. Pascal, J. Potier, D. J. Jones, J. Roziere and A. Michalowicz, *Inorg. Chem.*, *23* (1984) 2068; *24* (1985) 238.
16 T. Schleid and G. Meyer, *Z. Kristallogr.*, *186* (1989) 258; *Z. Naturforsch.*, *Teil B*, *44* (1989) 1007; *Z. Anorg. Allg. Chem.*, *583* (1990) 46.
17 G. Meyer, A. Lossin and T. Schleid, *Eur. J. Solid State Inorg. Chem.*, *28* (1991) 529.
A. Lossin and G. Meyer, *J. Less-Common Met.*, *175* (1991) 301–308.
18 M. Ciampolini, P. Dapporto and N. Nardi, *J. Chem. Soc.*, *Dalton Trans.*, (1979) 974.
19 M. Ciampolini, N. Nardi, R. Cini, S. Mangani and P. Orioli, *J. Chem. Soc.*, *Dalton Trans.*, (1979) 1983.
M. Ciampolini, C. Meali and N. Nardi, *J. Chem. Soc.*, *Dalton Trans.*, (1980) 376.
20 W. Biltz, *Raumchemie der festen Stoffe*, L. Voss, Leipzig, 1934.