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The influence of organic cations on the anionic structure of complex water containing lanthanide chlorides

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Abstract

In order to study the influence of organic cations on the anionic structure of complex water containing lanthanide chlorides, we prepared the following new compounds: (pyridinium)[$LnCl_4(H_2O)_2$] (Ln = La–Nd) [1,2], (4-picolinium)[$LnCl_4(H_2O)_3$] (Ln = La–Nd) [3], and (2-picolinium)[$LnCl_4(H_2O)_3$] (Ln = La–Nd). The crystal structures of the compounds have been determined on single crystals by X-ray methods.

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1. Introduction

From previous work on complex water containing lanthanide chlorides with organic cations such as $[(C_6H_5)_4E]MCl_4 \cdot 8H_2O$ (E = P, As; M = La–Gd) [4,5], $(CH_3NH_3)_3[LaCl_4(H_2O)_3]Cl_2$ [6], $(CH_3NH_3)_3[LnCl_4(H_2O)_2]Cl_2$ (Ln = Ce, Pr) [6,7], and $(CH_3NH_3)_8[NdCl_6][NdCl_4(H_2O)_2]_2Cl_3$ [8], we learnt the influence of the organic cations on the anionic structure. In order to study this in a more systematic way, we prepared the new compounds (pyridinium)[$LnCl_4(H_2O)_2$] (Ln = La–Nd), (4-picolinium)[$LnCl_4(H_2O)_3$] (Ln = La–Nd), and (2-picolinium)[$LnCl_4(H_2O)_3$] (Ln = La–Nd).

2. Synthesis

The compounds have been obtained by the reaction of $LnCl_3 \cdot xH_2O$ (Ln = La–Nd, $x = 6$–7) with pyridinium chloride and 4-picolinium chloride, respectively, in ethanol, and by the reaction of $LnCl_3 \cdot xH_2O$ (Ln = La–Nd, $x = 6$–7) with 2-picolinium chloride in an ethanol/butanol mixture. The compounds have been chemically analysed.

3. Results and discussion

The crystal structures of the compounds have been determined on single crystal X-ray diffraction data. The isotypic compounds (pyridinium)[$LnCl_4(H_2O)_2$] (Ln = La–Nd) crystallize with monoclinic symmetry, space group *C2/c*, $Z = 4$. The unit cell parameters are given in Table 1. The anionic structure is built up of $[LnCl_4(H_2O)_2]^-$-chains (Ln = La–Nd) along [0 0 1] (Fig. 1). In the case of (pyridinium)[$LaCl_4(H_2O)_2$] every lanthanum ion is surrounded by six chloride ions and two water molecules in the form of a distorted trigondodecahedron. The La–Cl distances are 293.5 pm (bridging chlorines) and 284.7 pm (terminal chlorines), and the La–H_2O distance is 251.3 pm. In the $[LaCl_4(H_2O)_2]^-$-chains the lanthanum ions are connected via two chlorine atoms. The motif of the packing of the chains may be considered as being a hexagonally close packing type. The chains are interconnected by hydrogen bondings creating channels in which the pyridinium cations are located (Fig. 2). The cations show rotational disorder at room temperature.

The similar structures of (4-picolinium)[$LnCl_4(H_2O)_3$] (Ln = La–Nd) and of (2-picolinium)[$LnCl_4(H_2O)_3$] (Ln = La–Nd) differ from the structure of the pyridinium complexes. The unit cell parameters are shown in Table 1.

The isotypic compounds (4-picolinium)[$LnCl_4(H_2O)_3$] (Ln = La–Nd) crystallize with triclinic symmetry, space group $P\bar{1}$, $Z = 2$. The characteristic unit of the structure is the dimeric complex anion $[Ln_2Cl_8(H_2O)_6]^{2-}$ (Ln = La–Nd) where two lanthanide atoms are linked via two chlorine atoms (Fig. 3). Every lanthanide ion is coordinated by five chloride ions and three water molecules in the form of a distorted trigondodecahedron. The dimers are interconnected via hydrogen bondings forming chains along [1 0 0] (Fig. 4). The chains are packed in a hexagonally close fashion. In the case of (4-picolinium)[$LaCl_4(H_2O)_3$], we find for the dimeric units La–Cl distances of 294.5 and 294.7 pm (bridging chlorines) and 286.7–289.2 pm (terminal chlorines) as well as La–H_2O distances of 249.2–258.3 pm. For the

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TABLE 1. Unit cell parameters

	a (pm)	*b* (pm)	*c* (pm)	*α* (°)	*β* (°)	*γ* (°)
(Pyridinium) $[LnCl_4(H_2O)_2]$ (Ln = La, Ce, Pr, Nd), space group *C*2/*c*, *Z* = 4						
Ln = La	1144.0(2)	1158.9(2)	943.0(2)		100.90(1)	
Ln = Ce	1139.3(3)	1155.7(3)	937.5(2)		100.77(2)	
Ln = Pr	1136.2(2)	1152.9(2)	934.1(1)		100.64(1)	
Ln = Nd	1131.9(2)	1149.6(3)	930.9(2)		100.60(2)	
(4-Picolinium) $[LnCl_4(H_2O)_3]$ (Ln = La, Cr, Pr, Nd), space group $P\bar{1}$, *Z* = 2						
Ln = La	729.6(1)	995.9(1)	1018.3(1)	72.55(1)	81.96(1)	87.76(1)
Ln = Ce	727.5(1)	993.2(1)	1013.4(1)	72.61(1)	81.95(1)	87.74(1)
Ln = Pr	725.3(1)	998.9(1)	1011.8(1)	72.49(1)	81.97(1)	87.66(1)
Ln = Nd	723.8(1)	986.6(1)	1010.2(1)	72.48(1)	81.95(1)	87.65(1)
(2-Picolinium) $[LnCl_4(H_2O)_3]$ (Ln = La, Ce, Pr, Nd), space group $P\bar{1}$ *Z* = 2						
Ln = La	734.7(1)	1002.6(1)	1014.1(1)	73.43(1)	86.35(1)	81.06(1)
Ln = Ce	732.1(1)	998.9(1)	1011.1(1)	73.46(1)	86.30(1)	81.00(1)
Ln = Pr	730.6(1)	996.8(1)	1009.5(1)	73.41(1)	86.22(1)	80.97(1)
Ln = Nd	728.5(1)	994.5(1)	1006.7(1)	73.40(1)	86.16(1)	80.96(1)

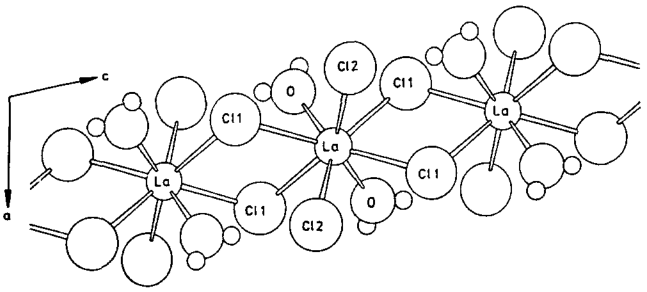

Fig. 1. $[LaCl_4(H_2O)_2]^-$-chain in (pyridinium)$[LaCl_4(H_2O)_2]$.

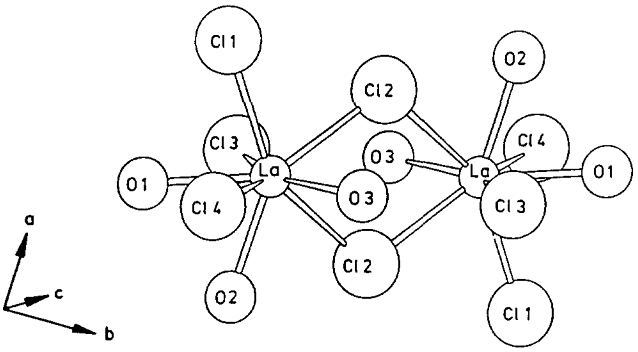

Fig. 3. Dimeric unit $[La_2Cl_8(H_2O)_6]^{2-}$ in (4-picolinium)-$[LaCl_4(H_2O)_3]$ and in (2-picolinium)$[LaCl_4(H_2O)_3]$.

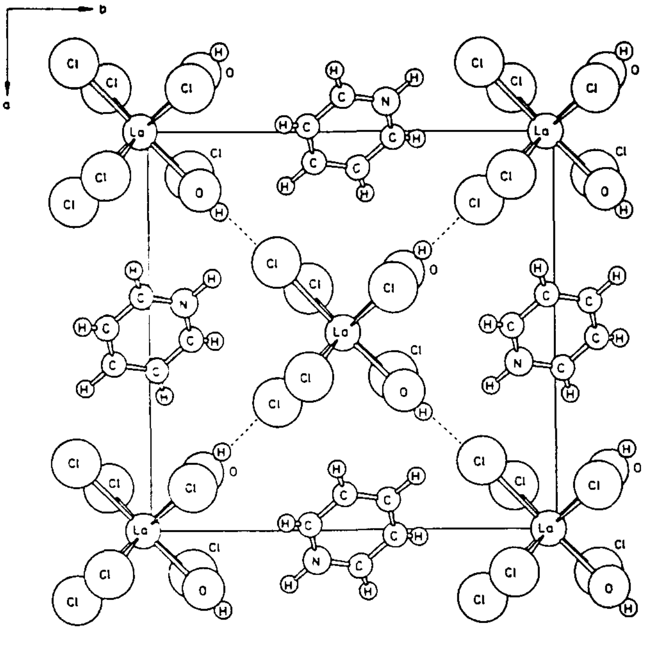

Fig. 2. Structure of (pyridinium)$[LaCl_4(H_2O)_2]$.

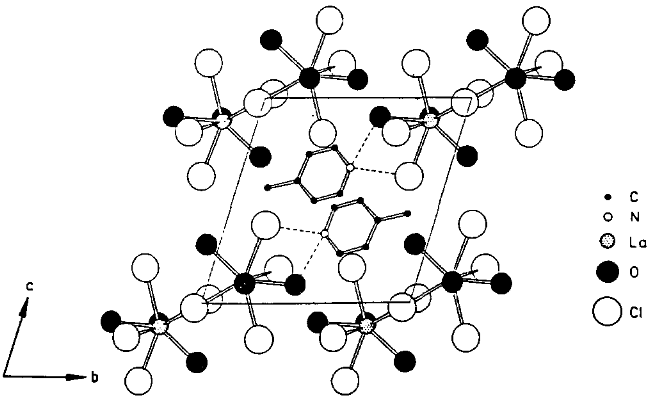

Fig. 4. Unit cell of (4-picolinium)$[LaCl_4(H_2O)_3]$, view along $[\bar{1}\,0\,0]$.

hydrogen bondings in the chains we find the distances Cl(1)–O(2) 307.9 pm, and Cl(2)–O(2) 316.5 pm, and between the chains the distances Cl(1)–O(1) 315.1 pm, Cl(4)–O(3) 318.7 pm, and Cl(3)–O(1) 317.9 pm. The 4-picolinium cations are linked to the dimers via a bifurcal hydrogen bonding between the N-atom of the cation and the terminal Cl(4)-atom and the O(1)-atom of a coordinated H_2O molecule (distances N–Cl(4) 322.7 pm, N–O(1) 313.5 pm).

The isotypic compounds (2-picolinium)[$LnCl_4(H_2O)_3$] (Ln = La–Nd) crystallize also with triclinic symmetry, space group $P\bar{1}$, $Z = 2$. We find the same dimeric units $[Ln_2Cl_8(H_2O)_6]^{2-}$ (Ln = La–Nd) as in (4-picolinium)[$LnCl_4(H_2O)_3$] (Ln = La–Nd) (Fig. 3) which are interconnected to chains via hydrogen bondings along [1 0 0] (Fig. 5). The chains are also packed in a hexagonally close fashion. In the case of (2-picolinium)[$LaCl_4(H_2O)_3$], we find La–Cl distances of 295.8 and 296.3 pm (bridging chlorines) and 284.7–288.6 pm (terminal chlorines) as well as La–H_2O distances of 252.9–260.9 pm (Fig. 3), and hydrogen bondings in the chains with the distances Cl(1)–O(2) 313.4 pm, and Cl(2)–O(2) 312.5 pm and between the chains with the distances Cl(1)–O(1) 324.9 pm, Cl(4)–O(3) 311.7 pm, and Cl(3)–O(1) 322.6 pm. In contrast to the 4-picolinium compounds, the 2-picolinium cations are linked to the dimers via a bifurcal hydrogen bonding between the N-atom of the cation and two terminal chlorine atoms (distances N–Cl(4) 332.2 pm, N–Cl(1) 326.1 pm).

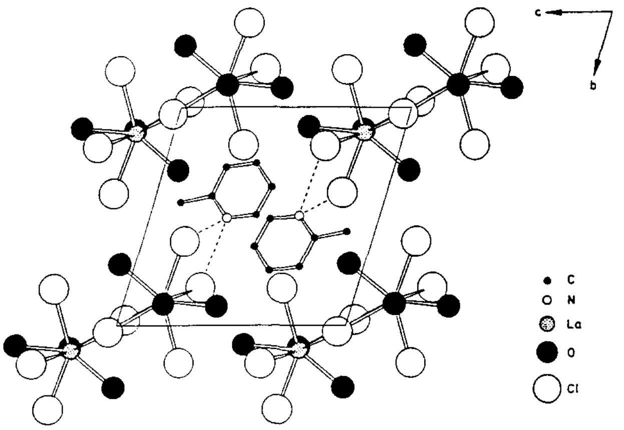

Fig. 5. Unit cell of (2-picolinium)[$LaCl_4(H_2O)_3$], view along [1 0 0].

From the structural investigations, we thus may conclude that in the presence of a symmetric unit like the pyridinium ion showing rotational disorder at room temperature, the formation of $[LnCl_4(H_2O)_2]^-$-chains (Ln = La–Nd) is possible. For packing reasons, these chains are structurally less flexible. The change to a less symmetric cation like 2-picolinium or 4-picolinium ion leads to a breakage of the chains and the formation of dimeric units $[Ln_2Cl_8(H_2O)_6]^{2-}$ (Ln = La–Nd). Compared to (2-picolinium)[$LaCl_4(H_2O)_3$] in 4-picolinium)[$LaCl_4(H_2O)_3$], the connection between the cation and the anionic dimer leads to a significant decrease in the angle Cl(4)–La–O(1) from 72.11° to 69.72° and an increase in the angle Cl(4)–La–Cl(1) from 79.02° to 82.25°.

The lanthanide compounds described are ideal systems to study the influence of minor changes of coordination geometry on magnetic and optical properties.

References

1 M. Schulze, D. Mackenstedt and W. Urland, *Acta Crystallogr., Sect. A, 46* (Suppl.) (1990) C-233.
2 M. Schulze and W. Urland, Dissertation Schulze, Universität Hannover, 1991.
3 D. Mackenstedt and W. Urland, *Z. Anorg. Allg. Chem., 619* (1993) 893.
4 W. Urland and U. Schwanitz-Schüller, *Angew. Chem., Suppl.* (1983) 1399.
5 W. Urland, *Z. Naturforsch., 40b* (1985) 496.
6 P. Runge and W. Urland, Dissertation Runge, Universität Hannover, 1990.
7 P. Runge, M. Schulze and W. Urland, *Z. Naturforsch., 45b* (1990) 603.
8 P. Runge, M. Schulze and W. Urland, *Z. Anorg. Allg. Chem., 592* (1991) 115.