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Brief Communications

Synthesis and structure of homochiral polymeric praseodymium tartrate*

M. S. Zavakhina,[a,b] M. P. Yutkin,[b,c] D. G. Samsonenko,[a,b] D. N. Dybtsev,[a,c] and V. P. Fedin[a,b]★

[a]A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
3 prosp. Akad. Lavrentieva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 330 9489. E-mail: cluster@niic.nsc.ru
[b]Novosibirsk State University,
2 ul. Pirogova, 630090 Novosibirsk, Russian Federation
[c]Division of the Advanced Materials Science, Pohang University of Science and Technology (POSTECH),
San 31, Hyojadong, Pohang, 790-784 Republic of Korea

The homochiral metal-organic coordination polymer of the composition $[\{Pr(H_2O)_2\}_2(\text{D-tart})_3]\cdot H_2O$ was synthesized by heating an aqueous solution of praseodymium(III) chloride and D-tartaric acid ($\text{D-}H_2\text{tart}$) in the presence of KOH. The crystal structure of the polymer was determined by X-ray crystallography and confirmed by IR spectroscopy, thermogravimetry, and elemental analysis.

Key words: praseodymium(III) complexes, coordination polymers, chiral complexes, tartaric acid, X-ray crystallography.

Enantiopure metal-organic coordination polymers have been extensively studied recently in view of their unique properties in stereoselective catalysis.[1,2] The limitless functional design of these structures has become possible by varying organic ligands and the nature of metal ions.[3,4] Due to wide coordination geometries of lanthanide ions, in particular, of the praseodymium ion, these cations can form various framework structures. In this case, natural polyfunctional acids, which are promising starting compounds for the synthesis of homochiral metal-organic compounds, can be used as organic ligands, because they are derived from natural products in optically pure form. The tartrate anion is a polyfunctional ligand and can be coordinated to metal ions in different fashion to form both mononuclear complexes and polymeric structures. The coordination chemistry of the tartrate ion is well known; however, three-dimensional praseodymium tartrate of the composition $[Pr_2(\text{D,L-tart})_3(H_2O)_3]\cdot 1.5H_2O$ (**1**) is the only structurally characterized representative of this class of compounds.[5] The latter complex contains the D,L-tartrate anion (*meso* form). In the present study, we report the synthesis, structure, and thermal stability of the new homochiral metal-organic coordination polymer

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$[\{Pr(H_2O)_2\}_2(D\text{-}tart)_3] \cdot H_2O$ (**2**) (H_2tart is tartaric acid) containing optically pure tartrate anions.

Results and Discussion

Coordination polymer **2** was synthesized in 79% yield by heating an aqueous solution of praseodymium(III) chloride and D-tartaric acid in the presence of potassium hydroxide. At 110 °C, intergrowths of pale-green elongated crystals were formed within 48 h. The synthesis in the absence of potassium hydroxide did not afford a solid product.

According to the X-ray diffraction data, compound **2** has a framework structure with space group $P2_12_12_1$. There are two crystallographically independent Pr^{3+} cations per asymmetric unit of **2**. The coordination polyhedra of Pr(1) and Pr(2) can be described as monocapped square antiprisms formed by nine oxygen atoms (Fig. 1). The coordination environment of the Pr(1) cation is formed by four carboxyl oxygen atoms of four tartrate anions, three hydroxyl groups, an two aqua ligands. The Pr(2) cation is surrounded by five carboxyl oxygen atoms of five tartrate anions, two hydroxyl groups, and two water molecules. The Pr—O bond lengths are in the range of 2.414(3)—2.640(3) Å. The praseodymium cations are linked by tartrate anions to form the neutral homochiral framework $[\{Pr(H_2O)_2\}_2(D\text{-}tart)_3]$ (Fig. 2). Compound **2** contains one water molecule of crystallization per formula unit.

The crystal structure of praseodymium tartrate $[Pr_2(D,L\text{-}tart)_3(H_2O)_3] \cdot 1.5H_2O$ (**1**) synthesized earlier also contains two praseodymium(III) cations. The coordination polyhedron of each cation is formed by nine oxygen atoms. The Pr(1) ion is coordinated to four tartrate anions through four carboxyl and three hydroxyl oxygen atoms. The Pr(2) ion is coordinated to five carboxyl and three hydroxyl oxygen atoms of five tartrate anions, the remaining coordination sites being occupied by water molecules. Therefore, all hydroxyl groups of the tartrate anions in compound **1** are coordinated to the praseodymium cations, whereas one hydroxyl group of each tartrate anion in compound **2** is uncoordinated and is involved in the formation of a hydrogen bond with a water molecule of crystallization (O(14)...O(1W), 2.675 Å).

Based on the X-ray diffraction, TGA, and elemental analysis data, the composition $[\{Pr(H_2O)_2\}_2(D\text{-}tart)_3] \cdot \cdot H_2O$ was assigned to compound **2**. The thermogravimetric analysis of compound **2** showed that there is 7.0% weight loss in the temperature range of 25—200 °C, which can be attributed to the removal of one water molecule of crystal-

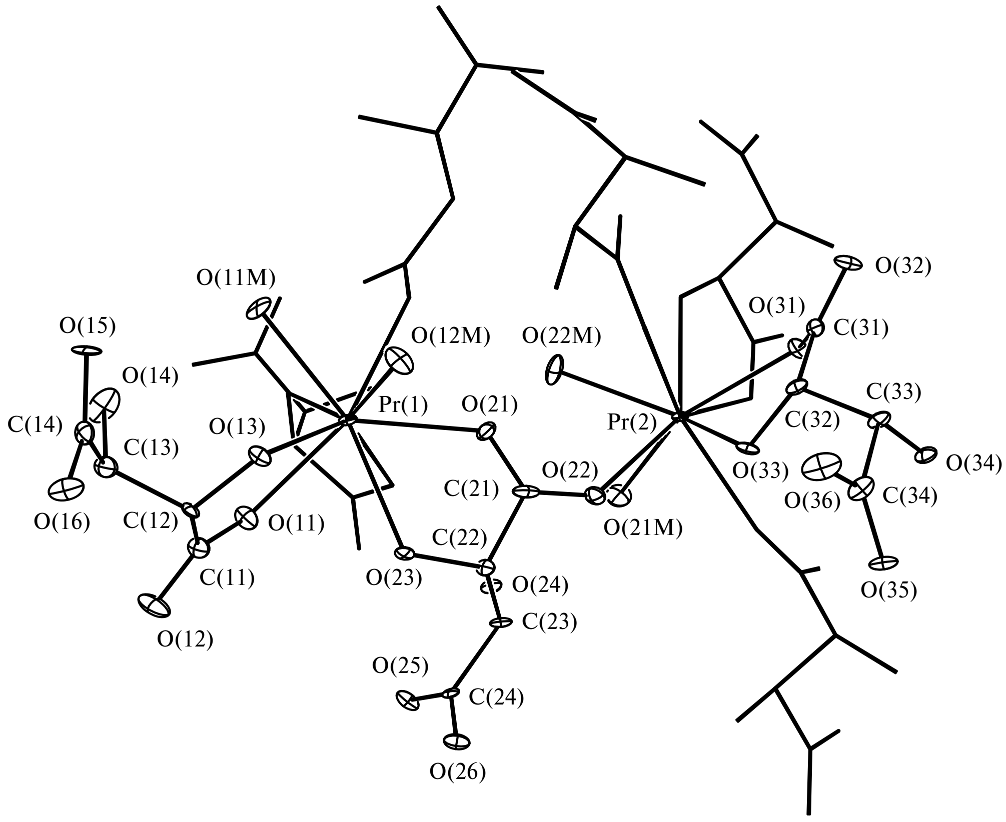

Fig. 1. Coordination environment of the Pr^{3+} cations in the crystal of **2**. Only crystallographically independent atoms are represented as displacement ellipsoids drawn at the 80% probability level.

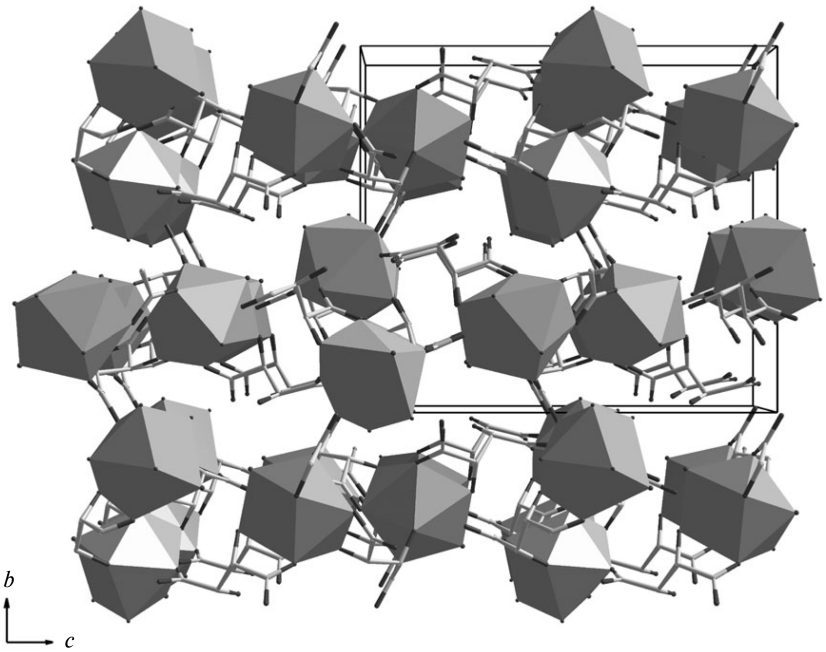

Fig. 2. Fragment of the metal-organic framework of **2** projected along the *a* axis. The coordination environment of the Pr^{3+} cations is represented by polyhedra.

lization and two coordinated water molecules (calculated for **2**, 6.6%). The onset of the decomposition of the metal-organic framework was observed at 250 °C.

Therefore, in the present study we synthesized and structurally characterized the new homochiral coordination polymer $[\{Pr(H_2O)_2\}_2(\text{D-tart})_3] \cdot H_2O$ having a framework structure.

Experimental

Starting D-tartaric acid, praseodymium(III) chloride, and potassium hydroxide were at least of a reagent grade. The IR spectra were recorded on a Scimitar FTS 2000 instrument in KBr pellets. The elemental analysis was carried out on an EURO EA 3000 instrument (EuroVector). The thermogravimetric analysis was performed on a TG 209 F1 thermobalance (Natzsch); the decomposition of the samples was carried out under argon atmosphere at a heating rate of 10 deg min^{-1}.

Catena{tritartratotetraaquadipraseodymium(III)} monohydrate, $[\{Pr(H_2O)_2\}_2(\textit{D}\text{-tart})_3] \cdot H_2O$ (2). A mixture of $PrCl_3 \cdot 7H_2O$ (0.112 g, 0.30 mmol), *D*-tartaric acid (0.045 g, 0.30 mmol), potassium hydroxide (0.028 g, 0.50 mmol), and H_2O (3.0 mL) was placed in a sealed glass tube and kept under temperature-controlled conditions at 110 °C for 48 h. The pale-green crystals that formed were washed several times with H_2O and dried in air. The yield was 0.065 g (79%). Found (%): C, 17.7; H, 2.6. $C_{12}H_{22}O_{23}Pr_2$. Calculated (%): C, 17.7; H, 2.7. IR: (KBr), ν/cm^{-1}: 480 (w), 521 (m), 554 (m), 614 (m), 707 (m), 791 (w), 840 (w), 826 (w), 894 (w), 1056 (m), 1085 (m), 1110 (m), 1148 (w), 1232 (m), 1253 (m), 1293 (m), 1322 (s), 1389 (s), 1412 (s), 1583 (s), 2652 (m), 2768 (m), 2930 (m), 3430 (m, sh). TGA: found Δm = 7.0%; calculated for $3H_2O$ 6.6%.

Table 1. Principal crystallographic data and the X-ray diffraction data collection and refinement statistics for coordination polymer **2**

Parameter	Characteristics
Molecular formula	$C_{12}H_{22}O_{23}Pr_2$
Molecular weight/g mol^{-1}	816.12
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	7.890(1)
b/Å	15.403(1)
c/Å	17.534(1)
V/Å^3	2130.9(3)
Z	4
ρ_{calc}/g cm^{-3}	2.544
μ/mm^{-1}	7.401
F(000)	1584
Crystal dimensions/mm	0.10×0.10×0.04
θ-Scan range/deg	2.10—40.75
Ranges of h, k, l indices	$-13 \le h \le 13$, $-24 \le k \le 24$, $-23 \le l \le 23$
Number of measured reflections	23363
Number of independent reflections	7404 (R_{int} = 0.0563)
Number of reflections with $F > 4\sigma(F)$	7222
Number of refined parameters	334
T_{max}/T_{min}	0.7562/0.5248
Goodness-of-fit on F^2	1.037
R factors $[F > 4\sigma(F)]$	R_1 = 0.0330, wR_2 = 0.0890
R factors (all reflections)	R_1 = 0.0340, wR_2 = 0.0896
Residual electron density (min/max)/e Å^{-3}	0.042(9) −3.270/1.907

Single-crystal X-ray diffraction study of compound **2** was performed at 100 K on an ADSC Quantum 210 automated one-circle diffractometer equipped with an area detector with the use of synchrotron radiation (λ = 0.85000 Å; Macromolecular Crystallography Wiggler Beamline 4A, Pohang Accelerator Laboratory). The X-ray intensity data were collected, frames were integrated, the X-ray data were processed, and the absorption correction was applied with the use of the HKL2000 program package.[6] The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters (except for hydrogen atoms) with the use of the SHELX-97 program package.[7] The hydrogen atoms of the CH groups of the tartrate anions were positioned geometrically and refined using a riding model. The hydrogen atoms of the water molecules and the OH groups of the tartrate anions were not located. The crystallographic data and the X-ray diffraction data collection and refinement statistics are given in Table 1. The complete tables of interatomic distances, bond angles, atomic coordinates, and displacement parameters were deposited to the Cambridge Crystallographic Data Centre (CCDC 825050) and can be obtained from the authors.

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References

1. L. J. Murray, M. Dinca, J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294.
2. J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670.
3. R. Robson, *J. Chem. Soc., Dalton Trans.*, 2000, 3735.
4. O. M. Yaghi, M. O´Keeffe, N. W. Ockwing, H. K. Chae, M. Eddaoudi, J. Kim, *Nature*, 2003, **423**, 705.
5. M. Athara, G. Lia, Z. Shia, Y. Chena, Sh. Feng, *Solid State Sciences*, 2008, **12**, 1853.
6. Z. Otwinowski, W. Minor, *Methods in Enzymology*, 1997, **276**, 307.
7. G. M. Sheldrick, *Acta Cryst.*, 2008, **64A**, 112.

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