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THE CRYSTAL AND MOLECULAR STRUCTURE OF PRASEODYMIUM(III) 2-FURAN CARBOXYLATE DIHYDRATE

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Praseodymium(III) 2-furanocarboxylate dihydrate is monoclinic, space group $P2_1/c$. The lattice parameters are $a = 10.349(2)$, $b = 16.727(3)$, $c = 9.458(1)$ Å, $\beta = 92.61(1)^\circ$. The crystal structure was solved and refined by a full-matrix least-squares method to $R = 0.034$ and $R_w = 0.039$ from 2333 reflections. Carboxylic ions bond in the complex as bidentates and as bi- and terdentate-bridging ligands. The water molecules bond to the metal. The coordination number of the praseodymium atom is nine. The coordination polyhedron is intermediate between a distorted tricapped trigonal prism and a distorted monocapped square antiprism.

Key words: Furanocarboxylic acid, lanthanides, praseodymium, complex, structure

INTRODUCTION

Praseodymium(III) 2-furanocarboxylate dihydrate was prepared by a double decomposition reaction by adding equivalent amounts of an ammonium pyromucate solution to a solution of praseodymium nitrate and crystallizing.¹ The prepared complex when heated in air loses its crystallization water in one step and then decomposes to Pr_6O_{11} through the intermediate consisting of unstable oxyppyromucate and $Pr_2O_2CO_3$.² A recorded diffractogram using the Debye-Scherrer method showed that the complex prepared was crystalline. It is characterized by low symmetry and a large unit cell.

Preliminary study of single crystals permitted the determination of the lattice parameters³ and to show that the praseodymium complex is isomorphic with the corresponding La and Ce(III) complexes.

On the basis of IR spectra it was found that the carboxylic ion occurs in the complex as a bidentate and a bridging ligand, and that crystallization water was inner sphere.¹ The aim at the work reported here has been to determine the complete crystal structure of praseodymium(III) 2-furanocarboxylate dihydrate and to describe the metal ion coordination geometry.

EXPERIMENTAL

Pale green crystals were grown from an aqueous solution. A single crystal with dimensions $0.4 \times 0.25 \times 0.18$ mm was used for data collection. Precise lattice parameters were obtained by least-squares refinement of 2θ values of 15 reflections centred on the diffractometer.

Crystal data: $Pr(C_5H_3O_3)_3 \cdot 2H_2O$, $M_w = 510.16$, $F(000) = 1000$, monoclinic, space group $P2_1/c$, $a = 10.349(2)$, $b = 16.727(3)$, $c = 9.458(1)$ Å, $\beta = 92.61(1)^\circ$, $V = 1635.5(4)$ Å³, $Z = 4$, $D_x = 2.07$ g cm⁻³, $D_m = 2.07$ g cm⁻³ (by flotation in bromobenzene/dibromoethane mixture), $\mu(MoK_\alpha) = 2.87$ mm⁻¹.

Intensities were measured at 19°C on a Syntex P2₁ diffractometer using graphite monochromatized MoK_α radiation and a θ - 2θ scan technique. Scan rates were dependent on the intensity of reflection and varied from 1.9 to 29.3° min⁻¹. No

stationary background measurements were made: the background and integrated intensity of each reflection was calculated by the Lehmann and Larsen⁴ profile-analysis method using the program PRARA.⁵ Two standard reflections, monitored every 75 reflections, showed intensity variation $\leq 5.36(I)$. 2838 independent reflections were collected in the 2θ range 3–50° and the hkl range: h 0–12, k 0–19, l ± 11 . 2333 reflections satisfying the criterion $F_o \geq 46(F)$ were used in the calculations. Lorentz and polarization corrections were applied to the data, but no correction was made for absorption.

The praseodymium position was found from a Patterson synthesis and the non-hydrogen atoms of ligands and water molecules were located by Fourier syntheses. All H-atoms were found on difference Fourier maps. Atomic coordinates and thermal parameters were refined by the full-matrix least-squares method. The function minimized was $\sum w(F_o - F_c)^2$, ($w = 1/6^2(F)$). Temperature factors for non-hydrogen atoms were refined anisotropically, whereas those of the H-atoms were treated isotropically. Three H-atoms were placed at fixed positions. Eight reflections having $\Delta/6 > 50$ were excluded from the last cycle of refinement. The isotropic extinction parameter x was refined to $x = 33.7(8) \times 10^{-8}$; F_o is multiplied by $(1-x F^2) \sin \theta$. The final R and R_w factors were 0.034 and 0.039, respectively. The final electron density map showed residual some peaks ($\Delta\rho_{\max} \leq 2.2 \text{ e}\text{\AA}^{-3}$) near the Pr atom. Structure was solved and refined using SHELX 76⁶; ORTEP II⁷ and PLUTO⁸ were used for crystal and molecular drawings.

Atomic positional and thermal parameters are given in Tables I and II. Lists of structure factors and anisotropic thermal parameters of the non-hydrogen atoms can be obtained from the Editor on request.

TABLE I
Final fractional coordinates and equivalent isotropic thermal parameters (\AA^2), $\text{UEQ} = (U_{11}^2 + U_{22}^2 + U_{33}^2)^{1/3}$ for the heavy atoms.

| Atom | x/a | y/b | z/c | UEQ |
|-------|------------|------------|------------|-----------|
| PR | 0.02009(4) | 0.13241(2) | 0.03546(4) | 0.0181(1) |
| OW(1) | 0.2372(5) | 0.0644(3) | 0.0321(5) | 0.030(2) |
| OW(2) | -0.0969(5) | 0.2649(3) | 0.0022(6) | 0.033(2) |
| O(1A) | -0.1418(5) | 0.1547(3) | 0.2356(5) | 0.028(2) |
| O(2A) | -0.2143(5) | 0.0922(3) | 0.0431(5) | 0.028(2) |
| C(1A) | -0.2297(7) | 0.1169(4) | 0.1683(7) | 0.022(2) |
| C(2A) | -0.3530(7) | 0.0989(4) | 0.2308(7) | 0.029(2) |
| C(3A) | -0.4477(7) | 0.0519(5) | 0.1799(8) | 0.032(3) |
| C(4A) | -0.5410(9) | 0.0496(6) | 0.283(1) | 0.048(4) |
| C(5A) | -0.5006(8) | 0.0956(6) | 0.390(1) | 0.044(3) |
| OA | -0.3814(5) | 0.1275(3) | 0.3593(6) | 0.047(2) |
| O(1B) | -0.0834(5) | 0.1250(3) | -0.2326(5) | 0.029(2) |
| O(2B) | -0.0090(5) | 0.0127(3) | -0.1342(5) | 0.023(2) |
| C(1B) | -0.0686(7) | 0.0502(4) | -0.2361(7) | 0.023(2) |
| C(2B) | -0.1189(7) | 0.0042(4) | -0.3580(7) | 0.021(2) |
| C(3B) | -0.1718(9) | 0.0233(5) | -0.4843(8) | 0.032(3) |
| C(4B) | -0.1974(8) | -0.0494(5) | -0.5571(8) | 0.034(3) |
| C(5B) | -0.1595(8) | -0.1079(4) | -0.4700(8) | 0.032(3) |
| OB | -0.1084(5) | -0.0777(3) | -0.3455(5) | 0.025(2) |
| O(1C) | 0.1505(5) | 0.2245(3) | 0.1787(5) | 0.028(2) |
| O(2C) | 0.1575(5) | 0.3026(3) | 0.3702(5) | 0.033(2) |
| C(1C) | 0.2070(7) | 0.2698(4) | 0.2657(7) | 0.021(2) |
| C(2C) | 0.3454(7) | 0.2859(4) | 0.2474(7) | 0.022(2) |
| C(3C) | 0.432(1) | 0.2585(7) | 0.158(1) | 0.044(3) |
| C(4C) | 0.5530(9) | 0.2922(6) | 0.198(1) | 0.046(4) |
| C(5C) | 0.5339(8) | 0.3387(6) | 0.307(1) | 0.044(3) |
| OC | 0.4079(5) | 0.3368(3) | 0.3416(5) | 0.036(2) |

TABLE II
Final fractional coordinates and isotropic temperature factors ($A^{\circ 2}$) for the hydrogen atoms.

| Atom | x/a | y/b | z/c | U |
|---------------------|------------|-----------|------------|---------|
| HW(11) [†] | 0.2364(0) | 0.0126(0) | 0.0140(0) | 0.12(4) |
| HW(12) [†] | 0.2876(0) | 0.1014(0) | -0.0440(0) | 0.13(4) |
| HW(21) | -0.104(8) | 0.300(5) | -0.075(8) | 0.05(2) |
| HW(22) | -0.090(8) | 0.288(5) | 0.098(9) | 0.06(3) |
| H(3A) [†] | -0.4744(0) | 0.0502(0) | 0.1050(0) | 0.03(2) |
| H(4A) | -0.62(1) | 0.034(6) | 0.26(1) | 0.08(3) |
| H(5A) | -0.544(8) | 0.113(5) | 0.472(8) | 0.05(3) |
| H(3B) | -0.179(9) | 0.068(6) | -0.52(1) | 0.07(3) |
| H(4B) | -0.228(8) | -0.052(5) | -0.650(8) | 0.04(2) |
| H(5B) | -0.148(8) | -0.168(5) | -0.471(8) | 0.05(2) |
| H(3C) | 0.41(1) | 0.235(6) | 0.12(1) | 0.05(4) |
| H(4C) | 0.626(7) | 0.287(4) | 0.162(7) | 0.03(2) |
| H(5C) | 0.602(9) | 0.358(5) | 0.372(9) | 0.06(3) |

[†] Position fixed.

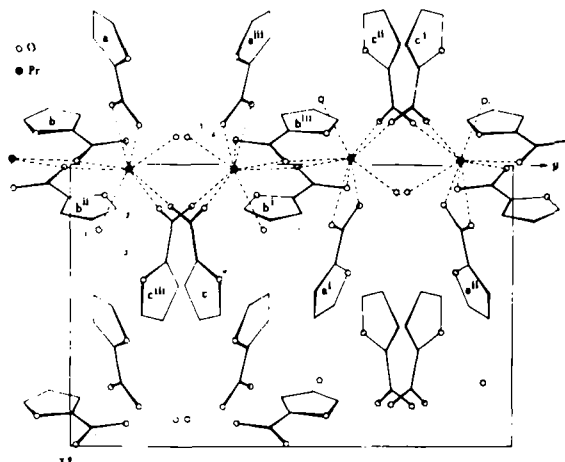


FIGURE 1 The crystal structure viewed along c ; (---) Pr-O bond, (...) hydrogen bond. Symmetry code: none: x, y, z (i): $x, 1/2 + y, 1/2 + z$; (ii): x, y, z ; (iii): $x, 1/2 - y, 1/2 + z$; (iv): $x, 1/2 - y, -1/2 + z$.

DISCUSSION

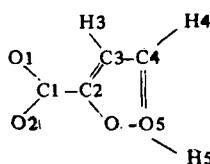
The structure in projection on the ab plane is given in Fig. 1. The Pr-O distances in the coordination sphere are presented in Table III and the ligand geometry in Table IV. The bond distances and angles in the three anions are comparable. The furan ring and carboxylic groups are planar within experimental error. The planes of the COO^- groups are twisted with respect to the furan ring in the several anions with angles of A $-7.4(9)$, B $-6.9(9)$, C $-4.7(9)^\circ$.

In the structure the praseodymium atoms are surrounded by two water molecules and three 2-furancarboxylic ligands. The central atoms are coordinated by oxygen atoms of carboxylic acid groups. Praseodymium(III) atoms are characterized by a coordination number of nine involving seven oxygen atoms of carboxylic acid ligands A, B, C and the two water molecules: O(W1) and O(W2). The structural functions of the

TABLE III
Bond lengths (Å) in the coordination polyhedron with estimated standard deviations in parentheses. For symmetry codes see Figure 1.

| | | | |
|------------------------|----------|-------------------------|----------|
| Pr-O(1A) | 2.612(5) | Pr-O(1C) | 2.422(5) |
| Pr-O(2A) | 2.522(5) | Pr-O(2C) ⁱⁱⁱ | 2.419(5) |
| Pr-O(1B) | 2.710(5) | Pr-OW(1) | 2.520(5) |
| Pr-O(2B) | 2.574(5) | Pr-OW(2) | 2.538(5) |
| Pr-O(2B) ⁱⁱ | 2.606(5) | | |

TABLE IV
Geometry of 2-furanocarboxylic acid anions and water molecules. Estimated standard deviations are given in parentheses.



| | anion A | anion B | anion C |
|-------------------------|-----------|----------------------|-----------|
| Bond lengths (Å) | | | |
| C(1)-O(1) | 1.257(8) | 1.261(8) | 1.244(8) |
| C(1)-O(2) | 1.271(8) | 1.284(8) | 1.260(8) |
| C(1)-C(2) | 1.462(10) | 1.462(10) | 1.475(10) |
| C(2)-C(3) | 1.329(11) | 1.330(11) | 1.343(11) |
| C(2)-O | 1.351(9) | 1.378(8) | 1.373(8) |
| C(3)-C(4) | 1.404(13) | 1.418(11) | 1.407(15) |
| C(3)-H(3) | 0.75 | 0.84 | 0.57 |
| C(4)-C(5) | 1.324(14) | 1.326(11) | 1.315(14) |
| C(4)-H(4) | 0.89(10) | 0.92(8) | 0.85(7) |
| C(5)-O | 1.388(10) | 1.366(9) | 1.358(10) |
| C(5)-H(5) | 0.96(8) | 1.01(8) | 0.97(9) |
| Bond angles (°) | | | |
| O(1)-C(1)-O(2) | 121.1(5) | 121.3(5) | 126.0(5) |
| O(1)-C(1)-C(2) | 121.6(5) | 120.2(5) | 117.6(5) |
| O(2)-C(1)-C(2) | 117.3(5) | 118.5(5) | 116.4(5) |
| C(1)-C(2)-C(3) | 128.2(6) | 134.3(6) | 133.8(7) |
| C(1)-C(2)-O | 121.3(5) | 115.5(5) | 117.9(5) |
| C(3)-C(2)-O | 110.4(6) | 110.1(6) | 108.2(7) |
| C(2)-C(3)-C(4) | 106.5(7) | 106.8(6) | 107.7(8) |
| C(3)-C(4)-C(5) | 108.2(8) | 106.7(7) | 106.6(8) |
| C(4)-C(5)-O | 108.4(7) | 110.8(6) | 110.8(7) |
| C(2)-O-C(5) | 106.5(6) | 105.5(5) | 106.7(6) |
| Water molecules | | | |
| OW(1)-HW(11) | 0.88 | <HW(11)-OW(1)-HW(12) | 115° |
| OW(1)-HW(12) | 1.10 | | |
| OW(2)-HW(21) | 0.93(8) | <HW(21)-OW(2)-HW(22) | 118.7° |
| OW(2)-HW(22) | 0.99(8) | | |

carboxylic group of the individual ligands are different. Carboxylic acid group A functions as a bidentate.

The oxygen atoms of carboxylic ligand B act as a bridging bidentate. The carboxylic

acid group of ligand C bridges two Pr(III) atoms related by the glide.

The Pr–O distances in the coordination sphere are similar to values found in other studied praseodymium complexes with organic ligands (carboxylic acids): 2.43(2)–2.90(2) Å in the diaquopraseodymium(III) nicotinate dimer,⁹ 2.44(1)–2.68(1) Å in bis(μ -acetato)bisureadi(acetato)praseodymium(III) urea dihydrate,¹⁰ ca 2.458 Å in the salt sodium triaqua(ethylenediaminetetraacetato)praseodymate(III) pentahydrate¹¹ and 2.34(2)–2.75(2) Å in tetraaquobis(hydrogeniminodiacetato)imino-diacetatodipraseodymium(III) dichloride trihydrate.¹²

The first two cited complexes are dimers, the third a monomer and the fourth has each coordination sphere joined three-dimensionally. The manner of Pr(III) coordination by the oxygen atoms of carboxylic acid groups of the 2-furanocarboxylic ligands are similar to the observed coordination in Pr(III) nicotinate.⁹ However the bridging ligands join Pr ions in layers.

The distances of Pr–O(W) bonds correspond to other values reported in the literature.¹¹ Templeton and coworkers¹¹ describe the nonacoordinate polyhedron of Lu(III) ions in complexes with organic ligands as a distorted tricapped trigonal prism or monocapped square antiprism. The coordination sphere and of coordination polyhedron of praseodymium(III) 2-furanocarboxylate dihydrate is shown in Fig. 2. The coordination polyhedron is intermediate between a distorted tricapped trigonal prism and a distorted monocapped square antiprism.

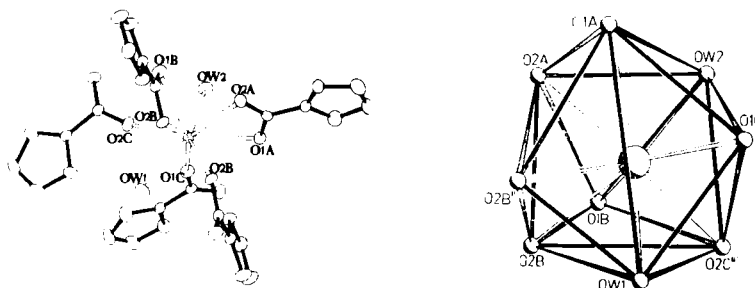


FIGURE 2 A perspective view of the coordination about the praseodymium(III) ion; a: ORTEP 30% probability thermal ellipsoid plot of the coordination sphere environment and (b): coordination polyhedron about the Pr(III) ion.

Bridging of Pr(III) ions occurs in two ways; one by ligand B and the other by ligand C. The ligand B (around the symmetry centre) joins polyhedra in pairs having a common edge. The bridging ligand C forms layers parallel to the *bc* plane.

In the coordination sphere are evident weak hydrogen bonds between water molecules and carboxylate groups of the ligands (distances 0 . . . 0 ca 2.721(7)–3.11(7)Å) and probably with the oxygen atom of furan ring C. Geometries of hydrogen bonds are

TABLE V
Geometry of the hydrogen bonds. Symmetry codes are given in Figure 1.

| D–H . . . A | D–A(Å) | D–H(Å) | H . . . A(Å) | D–H . . . A(°) |
|---|----------|---------|--------------|----------------|
| OW(1)–HW(11) . . . O(2A) ⁱⁱ | 2.721(7) | 0.88 | 1.85 | 171 |
| OW(1)–HW(12) . . . O(2C) ⁱⁱⁱ | 2.804(7) | 1.10 | 2.23 | 110 |
| OW(1)–HW(12) . . . OC ⁱⁱⁱ | 3.064(7) | 1.10 | 1.98 | 169 |
| OW(2)–HW(22) . . . O(1B) ⁱⁱⁱ | 3.110(7) | 0.99(8) | 2.16(8) | 161(5) |
| OW(2)–HW(21) . . . O(1A) ^{iv} | 2.877(7) | 0.93(8) | 1.97(8) | 164(5) |

given in Table V. Outer parts of ligands (furan rings) form a hydrophobic layer around the layers of the polycomplex. Only Van der Waals' interactions appear to be significant here.

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