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Short Note

$[Pr_2(pdc)_3(Hpdc)(H_2O)_4]_n \cdot n(H3hp) \cdot 8n(H_2O)$, a One-Dimensional Coordination Polymer Containing PrO_6N_3 Tri-Capped Trigonal Prisms and PrO_8N Mono-Capped Square Anti-Prisms (H_2pdc = Pyridine 2,6-Dicarboxylic Acid, $C_7H_5NO_4$; 3hp = 3-Hydroxy Pyridine, C_5H_5NO)

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Abstract: The synthesis, structure and some properties of the one-dimensional coordination polymer, $[Pr_2(pdc)_3(Hpdc)]_n \cdot n(H3hp) \cdot 8n(H_2O)$, ($H_2pdc$ = pyridine 2,6-dicarboxylic acid, $C_7H_5NO_4$; 3hp = 3-hydroxypyridine, C_5H_5NO) are described. One of the Pr^{3+} ions is coordinated by two O,N,O-tridentate pdc^{2-} ligands and one tridentate $Hpdc^-$ anion to generate a fairly regular PrO_6N_3 tri-capped trigonal prism, with the N atoms acting as the caps. The second Pr^{3+} ion is coordinated by one tridentate pdc^{2-} dianion, four water molecules and two monodentate bridging pdc^{2-} ligands to result in a PrO_8N coordination polyhedron that approximates to a mono-capped square-anti-prism. The ligands bridge the metal-atom nodes into a chain, which extends in the [100] direction. The $H3hp^+$ cation and uncoordinated water molecules occupy the inter-chain regions and an N–H···O and numerous O–H···O hydrogen bonds consolidate the structure. The $H3hp^+$ species appears to intercalate between pendant pdc rings to consolidate the polymeric structure. Crystal data: **1** ($C_{33}H_{43}N_5O_{29}Pr_2$), M_r = 1255.54, triclinic, $P\bar{1}$ (No. 2), Z = 2, a = 13.2567(1) Å,

b = 13.6304(2) Å, c = 13.6409(2) Å, α = 89.695(1)°, β = 63.049(1)°, γ = 86.105(1)°, V = 2191.16(5) Å^3, $R(F)$ = 0.033, $wR(F^2)$ = 0.084.

Keywords: one-dimensional coordination polymer; nine-coordination; praseodymium; intercalation

1. Introduction

Coordination polymers with potentially useful physical properties such as sorption and catalytic activity can be produced by careful choice of ligands, metal ions, the solvent and the pH of the solution [1–3]. Pyridine-2,6-dicaboxylic acid (H_2pdc, $C_7H_5NO_4$) is a versatile ligand that can chelate to, or bridge between, metal ions and can furnish different types of infinite-chain polymers [4–7]. As an extension of such studies, we now describe the solution-phase synthesis, crystal structure and characterization of the title compound, $[Pr_2(pdc)_3(Hpdc)]_n{\cdot}n(C_5H_6NO){\cdot}8n(H_2O)$, **1**, in which the two Pr^{3+} ions have very different coordination geometries. Previously reported complexes containing Pr^{3+} and de-protonated ligands derived from H_2pdc include $[Pr(pdc)(Hpdc)(H_2O)_2]_n{\cdot}nH_2O$ [8], $[Pr_2(pdc)_3(H_2O)_3]_n{\cdot}nH_2O$ [9], $[Pr_3(pdc)_4(Hpdc)(H_2O)_8]_n{\cdot}8nH_2O$ [9]. These show various ligand and water bonding modes to the metals, but all of them lead to nine-coordinate polyhedra for the metal atoms and the bridging ligands lead to infinite chains in the crystal.

2. Results and Discussion

2.1. Crystal Structure of ***1***

Compound **1** is a one-dimensional coordination polymer: The asymmetric unit contains two Pr^{3+} cations, three doubly-deprotonated $(C_7H_3NO_4)^{2-}$ (pdc^{2-}) dianions, one singly-deprotonated $(C_7H_4NO_4)^{-}$ ($Hpdc^{-}$) anion, one 3-hydroxylpyridinium ($H3hp^{+}$) cation and twelve water molecules (Figure 1).

The coordination geometries of the praseodymium ions in **1** are very different: Pr1 is coordinated by two O,N,O-tridentate pdc^{2-} dianions and the O,N,O-tridentate $Hpdc^{-}$ anion to generate a fairly regular tri-capped trigonal prismatic PrO_6N_3 coordination geometry with the N atoms serving as the caps protruding through the prismatic side-faces (Figure 2). Each ligand forms one Pr–O bond to the "top" triangular face and one to the bottom as well as the metal–nitrogen bond. The dihedral angle between the O1/O5/O11 and O3/O7/O9 triangular faces is 5.00(18)° and the metal ion is displaced by 1.6622(14) Å from the first triplet of O atoms and by −1.7184(14) Å from the second. The Pr–N bond lengths (Table 1) (mean = 2.606 Å) are longer than all but one of the Pr–O bonds (mean = 2.510 Å).

Figure 1. The asymmetric unit of **1** (50% displacement ellipsoids). The uncoordinated water molecules and the C-bound H atoms are omitted for clarity.

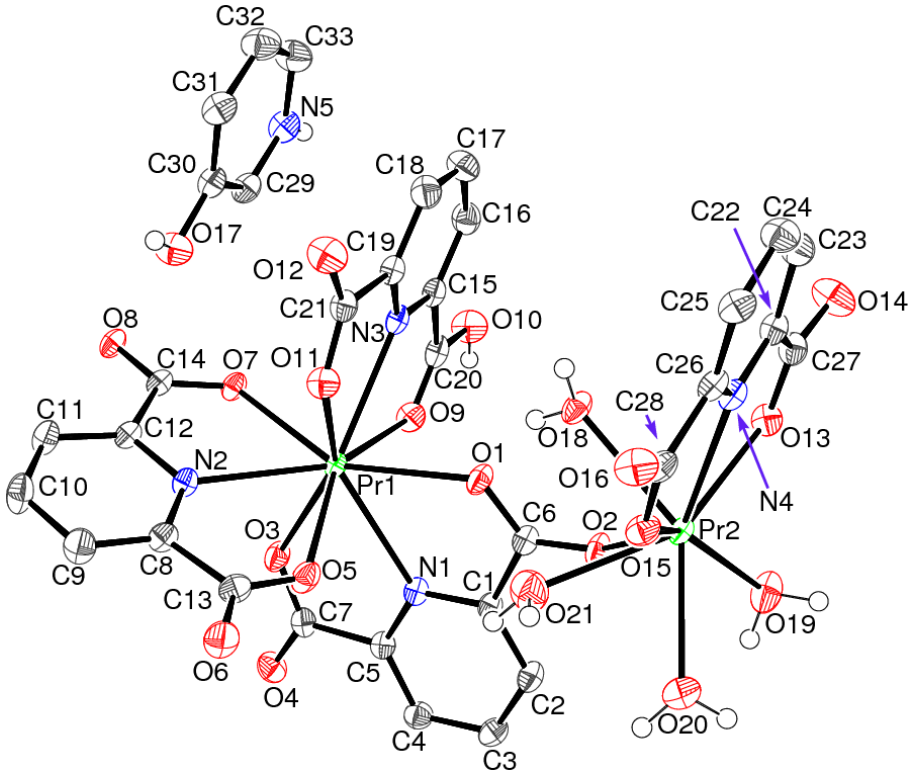


Figure 2. Detail of **1** showing the tri-capped trigonal prismatic coordination of Pr1 (50% displacement ellipsoids). The orchid-colored lines indicate the trigonal prism of O atoms.

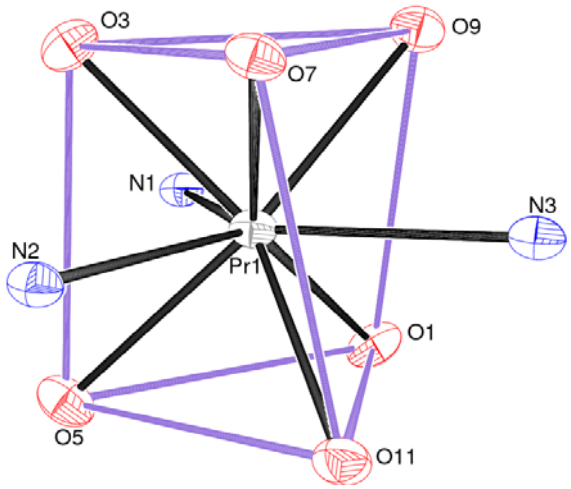


Table 1. Selected bond-distances (Å) in **1**.

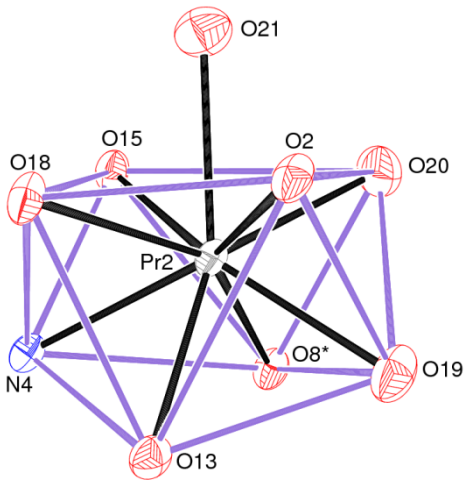
Pr1–O7	2.469(2)	Pr1–O11	2.472(2)
Pr1–O5	2.499(2)	Pr1–O3	2.501(2)
Pr1–O1	2.518(2)	Pr1–O9	2.601(2)
Pr1–N2	2.594(3)	Pr1–N1	2.604(3)
Pr1–N3	2.620(3)		
Pr2–O8 $^{\#1}$	2.448(2)	Pr2–O2	2.469(2)
Pr2–O15	2.477(2)	Pr2–O13	2.489(2)
Pr2–O19	2.490(3)	Pr2–O20	2.501(3)
Pr2–O18	2.525(2)	Pr2–O21	2.582(3)
Pr2–N4	2.604(3)		

Symmetry code: $^{\#1}$ $x-1, y, z$.

The geometrical parameters for the three chelating ligands (containing atoms N1, N2 and N3) are similar to those in related structures [6] and all the carboxylate groups are close to coplanar with their attached rings. The presence of the (un-removed) carboxylate proton in the N3-containing mono-ion is clearly indicated in terms of the C20–O10 and C20–O9 bond lengths of 1.291(4) Å and 1.231(4) Å, respectively.

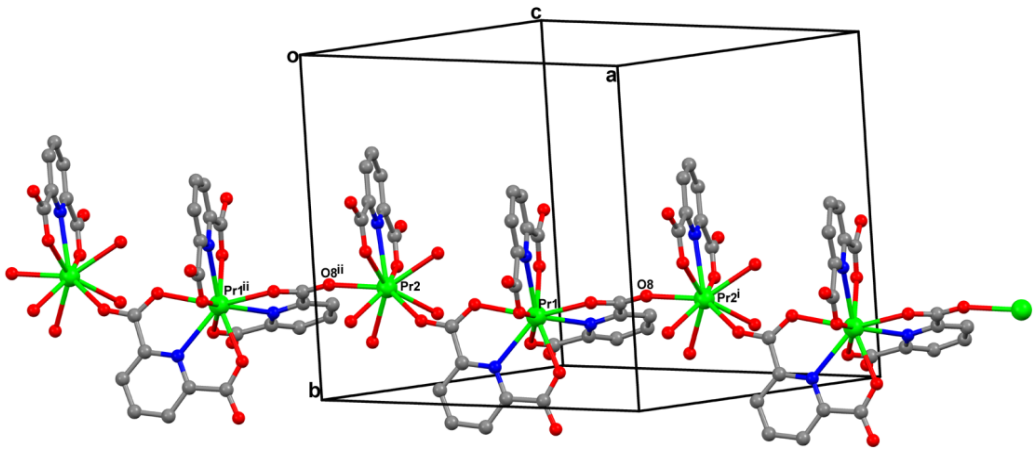
The Pr2 species in **1** is coordinated by an O,N,O-tridentate pdc^{2-} dianion (containing N4), four water molecules and two bridging monodentate-O pdc^{-} species to generate a PrO_8N coordination polyhedron that approximates to a mono-capped square anti-prism (Figure 3). The mean Pr–O separation is 2.498 Å and the four longer bonds are to the water molecules, although the differences are very small. The capping atom, O21, is part of a water molecule and protrudes through the O2/O15/O18/O20 square face of the anti-prism. The dihedral angle between this face and the O8/O13/O19/N4 face is 6.79(13)° and Pr2 is displaced from the two faces by −0.9083(13) Å and 1.5041(13) Å, respectively.

Figure 3. Detail of **1** (50% displacement ellipsoids) showing the mono-capped square anti-prismatic coordination of Pr2. O18, O19, O20 and O21 are parts of water molecules. The orchid lines indicate the square anti-prism. O8***** is generated by the symmetry operation ($x-1, y, z$).



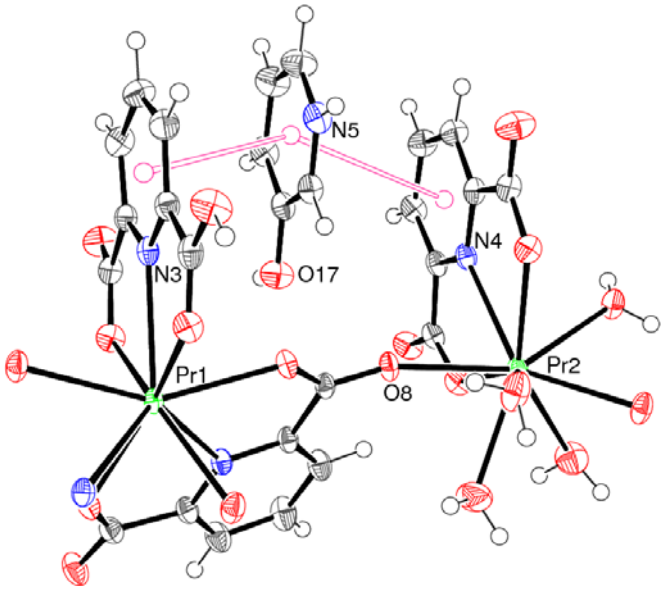
The bridging N1- and N2-containing pdc^{2-} dianions lead to infinite chains of alternating Pr1- and Pr2-centred polyhedra, which propagate in [100] (Figure 4). The Pr1···Pr2 separations are 6.4122(3) Å (via the N1 ligand) and 6.9775(3) Å (via the N2 ligand).

Figure 4. Fragment of a [100] chain of alternating Pr1- and Pr2-centred polyhedra in **1**.



To complete the structure of **1**, an N–H···O and numerous O–H···O and hydrogen bonds occur (see supplementary materials for a full list). The 3-hydroxypyridinium ($H3hp^{+}$) cation appears to play a significant role in establishing the structure of 1. As well as forming N–H···O and O–H···O hydrogen bonds, which serve to crosslink the [100] chains, it participates in two aromatic π–π stacking interactions (Figure 5). This might be described as an "intercalation" of the $H3hp^{+}$ species between the two pendant ligands (N3 attached to Pr1 and N4 attached to Pr2) of the alternating metal atoms in the chain.

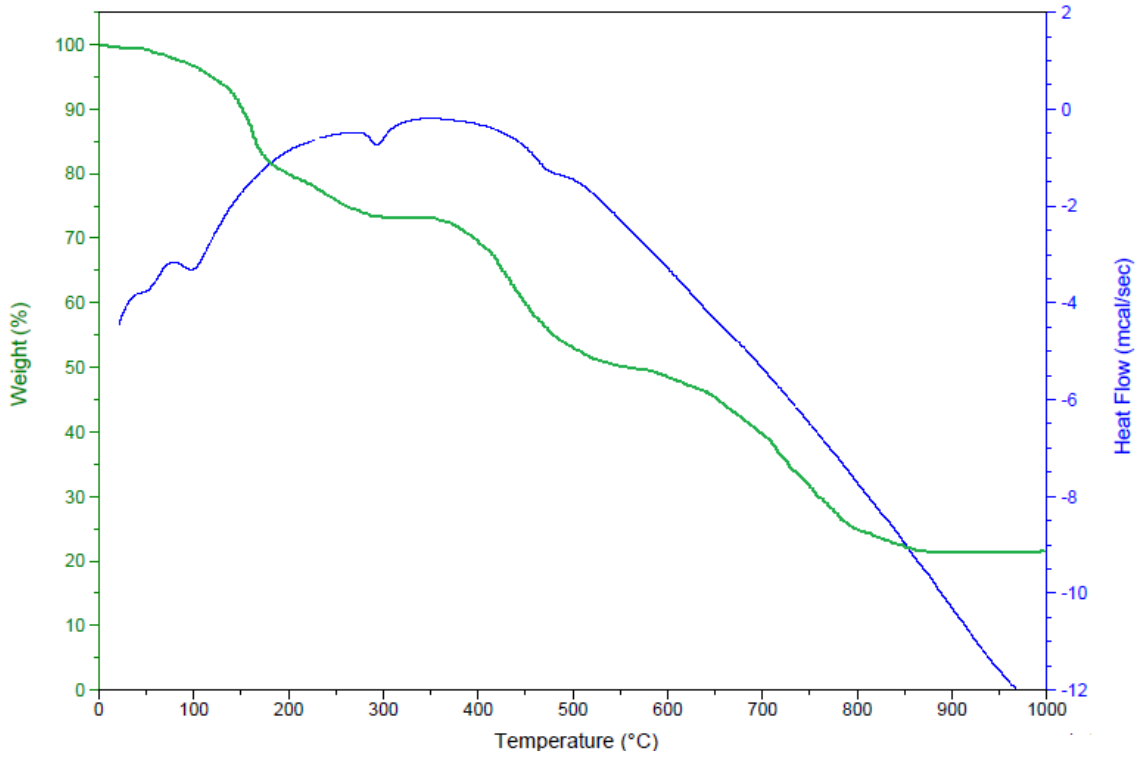
Figure 5. Fragment of the structure of **1** showing the π–π stacking interactions (open pink lines) of the "intercalated" $H3hp^{+}$ cation: The separations of its ring centroid with those of the N3- and N4-containing rings (indicated by pink spheres) are 3.596(2) Å and 3.647(3) Å, respectively.



2.2. Thermal Analysis

The TGA results (Figure 6) are consistent with the stoichiometry of the crystal: The first weight loss of about 17.8% (calculated value 17.2%) corresponds to the loss of the four coordinated and eight non-coordinated water molecules between 75 and 190 °C. The second weight loss of 7.6% up to 280 °C results from the removal of the 3-hydroxypyridinum ion (calcd. 7.2%). The third weight loss of about 49.4% is due to successive release of decomposition products from the pyridine dicarboxylate anions (calcd. 49.1%), yielding Pr_2O_3 as the final product (25.3% residual weight; calc. 26.5%).

Figure 6. TGA trace for **1**.



3. Experimental Section

3.1. Instrumental

The C, H, N elemental analysis was carried out with a Vario Micro Cube (Elementar, Germany). IR data (KBr pellet) were recorded on a Perkin–Elmer FTIR 180 spectrophotometer over the range 4000–400 cm^{-1}. TGA data (25–1000 °C) were recorded under continuous nitrogen flow, with a ramp-rate of 10 °C·min^{-1} using a SDT Q600 instrument (TA Instruments, USA).

3.2. Synthesis

A mixture of pyridine 2,6-dicarboxylic acid (84 mg, 0.5 mmol), 3-hydroxypyridine (45 mg, 0.5 mmol), $PrCl_3 \cdot 6H_2O$ (45 mg, 0.125 mmol) and 0.2 mL formic acid and 7 mL distilled water was sealed in a 23 mL Teflon-lined autoclave and heated to 170 °C for 12 h and cooled to room temperature at

30 °C·h^{-1} to yield a green solution. Green needles of **1** slowly grew as the water evaporated over two weeks and were recovered by vacuum filtration, rinsing with water and dried at room temperature. Analysis (%) calc. for $C_{33}H_{43}N_5O_{29}Pr_2$: N 5.58; C 31.54; H 3.43; Found: N 5.69; C 31.73; H 3.61. Yield *ca*. 65%. IR (cm^{-1}): 3572–3288 (broad, strong) water O–H stretch; 1630 ν_{asym}(C=O); 1415, 1359 ν_{sym}(C=O).

3.3. Single-Crystal Data Collection and Analysis

The single-crystal data for **1** (green needle 0.40 × 0.05 × 0.05 mm) were collected using a Bruker Kappa APEX II [10] CCD diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) at room temperature. Data reduction with SAINT [10] then proceeded and the structure was solved by direct methods with SHELXS [11]. The resulting atomic model was developed and refined against $|F|^2$ with SHELXL [11] and the "observed data" threshold for calculating the $R(F)$ residuals was set as $I > 2\sigma(I)$. The C- and N-bound bound H atoms were placed in idealised locations (C–H = 0.96–0.97 Å, N–H = 0.86 Å) and refined as riding atoms. The O-bound H atoms were located in difference maps and refined as riding atoms in their as-found relative locations. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) was applied in all cases. The structural model was analysed and validated with PLATON [12] and full refinement details are given in the deposited cif.

Crystal data for **1**: $C_{33}H_{43}N_5O_{29}Pr_2$, M_r = 1255.54, triclinic, $P\bar{1}$ (No. 2), Z = 2, a = 13.2567(1) Å, b = 13.6304(2) Å, c = 13.6409(2) Å, α = 89.695(1)°, β = 63.049(1)°, γ = 86.105(1)°, V = 2191.16(5) Å^3, $F(000)$ = 1252, T = 293(2) K, ρ_{calc} = 1.903 g·cm^{-3}, μ = 2.304 mm^{-1}, 18565 reflections recorded (6.0° ≤ 2θ ≤ 55.0°; −17 ≤ h ≤ 16, −17 ≤ k ≤ 17, −17 ≤ l ≤ 17), R_{Int} = 0.021, 9996 merged reflections, 8617 with $I > 2\sigma(I)$, 622 variable parameters, $R(F)$ = 0.033, $wR(F^2)$ = 0.084, $w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 3.8222P]$, where $P = (F_o^2 + 2F_c^2)/3$, min./max. $\Delta\rho$ = −1.06, +2.32 e Å^{-3}. Cambridge Structural Database deposition number: CCDC-885694.

4. Conclusions

The synthesis and crystal structure of the title one-dimensional coordination polymer have been described, in which the coordination polyhedra of the two nine-coordinate praseodymium ions are very different. The "guest" 3-hydroxypyridinium cation appears to play an important role in establishing the structure in terms of inter-chain hydrogen bonds and intra-chain intercalated π–π stacking interactions.

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