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Notes

Synthesis and crystal structure of a new acetate bridged metal-organic framework constructed by Pr (III) with 5-aminoisophthalic acid-$[Pr(CH_3COO)(AIP)(H_2O)_2]_n.nH_2O$

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A novel acetate bridged lanthanide complex $[Pr(CH_3COO)(AIP)(H_2O)_2]_n{\cdot}nH_2O$ (PAIT) (H2AIP=5-aminoisophthalic acid) has been synthesized at room temperature by gel diffusion technique using hydro silica gel and structurally characterized by single crystal X-ray diffraction (CIF file CCDC no. 1857252). The title compound crystallizes in monoclinic space group, $P2_1/c$ with a=10.5618(8) Å, b =12.1510(9) Å, c =10.7510(9) Å, α =90°, β =94.696(6)° , γ=90°. The Pr^{3+} ion has been coordinated by O_9 donor sets to form distorted tricapped triagonal prism geometry. Its structure features a 3D polymeric network possessing 'S' shaped hydrophilic pores.

Keywords: Metal-organic framework, Gel diffusion technique, 5-Aminoisophthalic acid, Praseodymium complex

Design and synthesis of porous metal organic frameworks (MOFs) have received enormous attention over past decades owing to their intriguing structural topologies and potential applications as functional crystalline materials**.** Tunable porosity, extra high surface area and high degree of crystallinity of some MOFs make them superior to conventional porous materials for a wide range of applications such as gas storage/separation, heterogeneous catalysis and ion exchange[1-4]. Among these materials, lanthanide MOFs (Ln-MOFs) in which trivalent lanthanide ions are connected by multi-topic aromatic linker have garnered immense interest as their unique chemical, optical and magnetic properties can be coupled with porosity features to produce novel materials. These inimitable features have enabled Ln-MOFs to be very promising candidates in the field of bioimaging, molecular /luminescence/fluorescent pH sensing[5-8]. Aromatic carboxylic acids have been preferentially selected as suitable connectors for the construction of Ln-MOFs, due to their ability to aggregate metal ions into M-O-C clusters, referred to as secondary building units (SBUs) which can act as rigid entities to form a stable architecture. Among the rigid polycarboxylic acids, 5-aminoisophthalic acid (H_2AIP) is emerging as an excellent structured motif for assembling different discrete SBUs for the construction of wide variety of Ln-MOFs because of its rich coordination modes together with an amino group intended to occupy the cavities of the expected networks[9,10]. This uncoordinated amino group can be subjected to post - synthetic modifications for obtaining functionalized MOF with tailored properties[11-13]. Considering all these versatile properties, we have selected H_2AIP for the preparation of the title compound.

Several coordination polymers involving lanthanide ions and H_2AIP ligands have already been reported[14-18] while those containing lanthanide ions and mixed-carboxylates are far less common[19-22]. Having studied the literature, few reports of Pr^{3+} ion based complexes of H_2AIP were found. Among them $[Pr_2(AIP)_3H_2O].3H_2O$ and $[Pr_2(H_2AIP(AIP)NO_3].8H_2O$ prepared by hydrothermal methods form an open 3D coordination framework with an uncoordinated amino group pointing into the channel structure, whereas in the complex $[Pr(\mu_2\text{-}OH)(AIP)]$, the amino group of the organic linker coordinates with the metal centre[23,24].

In the present work, the crystal growth of a novel 3D coordination polymer containing Pr^{3+}ion and H_2AIP building blocks, namely $[Pr(CH_3COO)(AIP)(H_2O)_2]_n{\cdot}$ nH_2O (grown by single gel diffusion technique) is reported. To the best of our knowledge, this is the first report of the complex of praseodymium with H_2AIP and bridging acetate ligand. The title compound is isostructural with the reported cerium complex of H_2AIP[25]. Our attempt to grow acetate bridged lanthanide MOFs of other lanthanides with 5-aminoisophthalic acid has not been successful. The grown crystals were characterized by elemental analysis, FT-IR and UV-Vis spectral studies, thermogravimetry, and single crystal X-ray diffraction studies.

Experimental

All the reagents and chemicals were of AR grade and used as such without further purification. 5-aminoisophthalic acid (Sigma Aldrich), praseodymium (III) nitrate hexahydrate (Alfa Aesar), sodium metasilicate (CDH) and glacial acetic acid (CDH) were purchased commercially. The percentage of carbon, hydrogen and nitrogen in the grown crystal was determined using Elementar Vario-EL 111 CHNS analyzer. The FT-IR spectrum was recorded with KBr pellets in the frequency range 4000-400 cm^{-1} using Thermo Nicolet, Avatar 370 spectrometer. The UV-Vis absorbance spectrum was recorded in the range 200–1200 nm with a Varian Cary 5000 UV-Vis-NIR spectrometer. Single crystal XRD analysis of the grown crystal was carried out using a Bruker AXS Kappa Apex2 CCD diffractometer, with graphite monochromated Mo Kα (λ= 0.71073 Å) radiation. The unit cell dimensions and intensity data were collected at 296 K. The program SAINT/XPREP was used for data reduction and APEX2/SAINT for cell refinement. The structure was solved with direct methods using SIR92 and refinement was carried out by full-matrix least squares on F^2 using SHELXL-2014/7 software[26]. All the non hydrogen atoms were refined anisotropically. Molecular graphics tool used was DIAMOND Version 3.1f[27]. Thermogravimetric analysis was carried out on Perkin Elmer Diamond TG/DTG analyzer instrument with a heating rate of 10 °C/min in nitrogen atmosphere. Magnetic susceptibility measurements were carried out on Sherwood scientific susceptibility balance Mk 1.

Single crystals of PAIT were grown by slow diffusion technique using sodium metasilicate (SMS) gel at room temperature[28,29]. It is an alternative technique to solution growth with controlled diffusion of metal ions through the gel to obtain good quality crystals. Sodium metasilicate was dissolved in double distilled water and filtered to obtain a clear solution. The density of solution was varied in the range 1.03–1.05 g cm^{-3}. H_2AIP of desired molarity (0.20–0.50 M) was incorporated within the gel and the pH of the gel was adjusted between 5.5–6.5 by adding acetic acid drop by drop with continuous stirring so as to get a homogenous solution. These solutions of different pH were transferred to various glass tubes and sealed properly to avoid contamination and allowed to set at room temperature. After proper setting of the gel, 5 mL of $Pr(NO_3)_3.6H_2O$ solution (0.20–0.5 M) is added carefully through the sides of the glass tube without tampering the surface of the gel and the glass tubes were kept undisturbed. Pale green- block shaped single crystals appeared at the gel solution interface after two days at pH 5.5 with 0.25 M concentration of both reagents and a gel density of 1.04 g cm^{-3}. The grown crystals were separated, washed with water and dried. The crystals obtained are stable in air and insoluble in common solvents. Elemental Analysis calculated for $C_{10}H_{14}NO_9Pr$ (%):C, 27.72; H, 3.25; N, 3.23. Found (%): C, 26.78; H, 3.09; N, 3.22. IR: (ν, cm^{-1}): 3460, 3342 ν_{str} (N-H); 1549 (ν_{as} COO^-); 1410 (ν_s COO^-); 1380 (ν_{str} C-N).

Results and Discussion

The FT-IR spectrum is shown in Supplementary data, Fig. S1.The presence of broad bands in the range 3550–3300 cm^{-1} is due to (ν O-H) of coordinated and lattice water molecules. Absence of multiple peaks in the range 3000–2500 cm^{-1} (ν O-H) and in the range 1700–1690 cm^{-1} (νCOOH) confirms that H_2AIP ligand is completely deprotonated and the carboxylate O atoms are coordinated to the central metal ion[30]. The corresponding asymmetric ($\nu_{as}COO^-$) and symmetric (ν_sCOO^-) stretching frequencies of the carboxylate ion at 1539 and 1410 cm^{-1} respectively support this observation. A sharp peak at 779 cm^{-1} may be due to C-H out of plane bending vibrations of aromatic ring[31, 32]. These characteristic absorption bands are in accordance with the result of single crystal X-ray diffraction analysis.

Single crystal X-ray diffraction study reveals that the title compound crystallizes in monoclinic space group, $P2_1/c$. The unit cell parameters are a=10.5618(8) Å, b =12.1510(9) Å, c =10.7510(9) Å, α=90°, β=94.696(6)°, γ=90°. Structure refinement parameters and details of crystal data are shown in Table 1.

The asymmetric unit of the crystal comprises of one crystallographically independent Pr^{3+}ion, one AIP^{2-} anion, one acetate ion, two aqua ligands and one lattice water molecule (Supplementary data, Fig. S2). Coordination environment of PAIT is shown in Fig.1. From the figure it is clear that, each Pr^{3+} ion is coordinated by nine oxygen atoms, four from three different H_2AIP ligands (O_1,O_2,O_3 and O_4) , two from two water molecules (O_7 and O_8), two from bidentate acetate (O_5,O_6) and one from monodentate acetate groups (O_5). As observed in the previously reported lanthanide complexes, the substituent NH_2 group in the organic linker does not coordinate with the central metal ion. It is noticeable that two of the three carboxylate group from H_2AIP linker (O_1,O_2) adopts bis monodentate coordination mode and the remaining one is chelate (O_3,O_4).

The selected bond lengths and bond angles are shown in the Supplementary data, Table S1. The Pr-O bond distances for carboxylate oxygens are in the range 2.380(4) to 2.668(3) Å and Pr-O_w bond lengths are

2.521(3) and 2.584(4) Å respectively. The carboxylic group chelated to Pr^{3+} gives rise to a four membered ring with a chelated angle of 51.34 (11)° for O(3)#1-Pr(1)-O(4)#1 and 49.10(10)° for O(6)#2-Pr(1)-O(5)#2 formed by bidentate acetate moiety.The O-Pr-O bond angles ranging from 49.10(10)° to 146.87(12)° are consistent with previously reported structures $[Pr_2(H_2AIP)_2(AIP)(NO_3)_2].8H_2O$ and $Pr(\mu_2\text{-}OH)(AIP)$. In the present case, the Pr^{3+} possesses an O_9-coordination sphere and coordination geometry can be best explained as distorted tri-capped trigonal prism[33]. The structure of polyhedra with open faces is shown in Supplementary data, Fig. S3.

In this compound each H_2AIP ligand shows μ_3- coordination mode linking three metal atoms, in which one of the carboxylic group forms a bis monodentate coordination bridging two neighbouring Pr^{3+} ions with a bond distance $Pr–O_1$= 2.380 Å and $Pr–O_2$= 2.392 Å and the second one is chelated to another Pr^{3+} ion with a bond distance $Pr–O_3$= 2.521 Å and $Pr–O_4$= 2.577 Å (Supplementary data, Fig. S4a).The acetate moiety present in the compound adopts μ_2-η^1: η^2 bonding mode connecting two neighbouring metal centres to form dimers with Pr·····Pr nonbonding distance 4.4372(2) Å (supplementary data, Fig. S4b). These discrete dimers (SBUs) are further connected by AIP^{2-} via μ_2 bridging manner to form a zigzag chain. Structural description of a simplified zig zag chain formed by discrete dimers (SBUs) is shown in Supplementary data, Fig. S5.

Table 1 — Crystallographic data and Structure refinement parameters of PAIT

Parameters	Value
Empirical formula	$C_{10} H_{14} N O_9 Pr$
Formula weight	433.13
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 10.5618(8) Å, α= 90°. b = 12.1510(9) Å, β= 94.696(6)° c = 10.7510(9) Å, γ = 90°.
Volume	1375.11(19) $Å^3$
Z	4
Density (calculated)	2.092 Mg/m^3
Absorption coefficient	3.588 mm^{-1}
$F_{(000)}$	848
Crystal size	0.100 × 0.100 × 0.050 mm^3
Theta range for data collection	2.534 to 24.998°.
Reflections collected	15777
Independent reflections	2426 [R_{int} = 0.0706]
Completeness to theta = 24.998°	100.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6524
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2426 / 14 / 222
Goodness-of-fit on F2	1.035
Final R indices [I>2sigma(I)]	R_1 = 0.0294, wR_2 = 0.0456
R indices (all data)	R_1 = 0.0496, wR_2 = 0.0516
Largest diff. peak and hole	0.717 and -0.597 e.$Å^{-3}$

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

The reverse arranged μ_3-H_2AIP ligand interconnects the zigzag chains in different directions extending the structure into a 3D polymeric network as shown in Fig. 2.

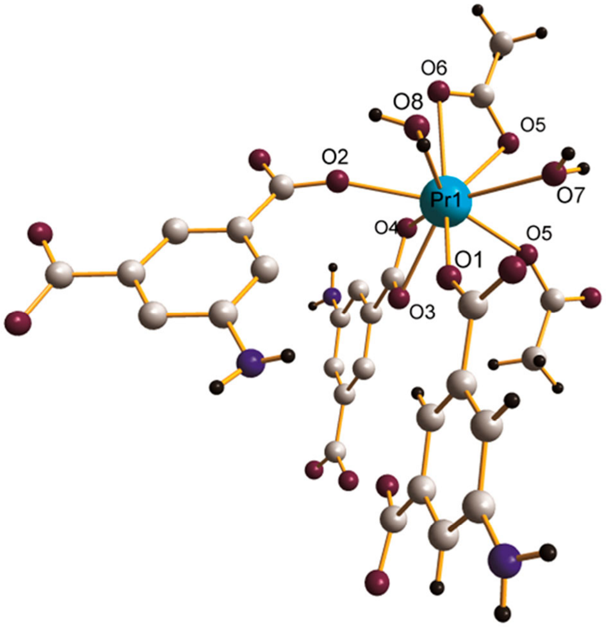

Fig. 1 — Coordination environment of Pr^{3+} ion in $[Pr(CH_3COO)(AIP)(H_2O)_2]_n.nH_2O$.

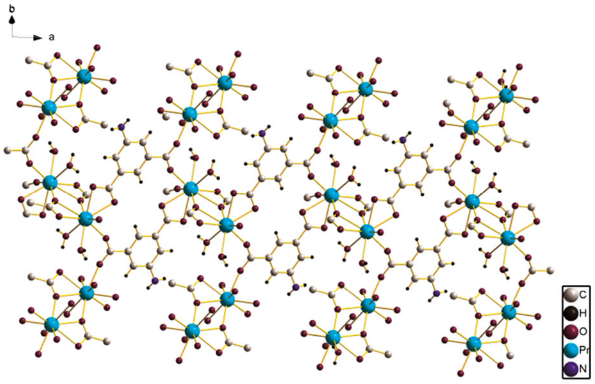

Fig. 2 — Perspective view of polymeric structure of PAIT along the 'c' axis.

Packing diagram in polyhedral designs viewed along ‘a’ axis in Fig. 3 shows the presence of ‘S’ shaped pores in the compound. The presence of entrapped water molecules inside the pores shows its hydrophilic nature[34].

The presence of extensive hydrogen bonding provides additional stability for the supramolecular framework. A detailed summary of geometrical data of hydrogen bonds are given in Supplementary data, Table S2. Three types of hydrogen bonding interactions are found within the network structure of PAIT. First is the intermolecular hydrogen bonding which exists between coordinated water molecules and the oxygen atoms of carboxyl group from both acetate moiety and H_2AIP ligands [(O(7)-H(7A)...O(6)#6,O(7)-H(7B)...O(4)#7,O(8)-H(8A)...O(4)#8]. The lattice water molecules form hydrogen bonds with oxygen atoms of coordinated water molecules [O(9)-H(9A)...O(8), O(9)-H(9B)...O(7)#6]. In addition to this N (1) atom of uncoordinated amino group of organic linker is involved in hydrogen bonding with lattice water molecules [O(9)-H(9A)...O(8),O(9)-H(9B)...O(7)#6)]. The hydrogen bonding interactions are shown in Fig. 4.

Thermal stability of the compound has been investigated in nitrogen atmosphere at a heating rate of 10 °C min^{-1} in the temperature range 40-870 °C. The TGa (curve 1) and DTG (curve 2) of the compound are shown in the Supplementary data, Fig. S6. At first, dehydration process occurs and corresponding weight loss of about 12.08% (calculated 12.44%) is observed in the temperature range of 95-180 ºC which can be attributed to the loss of both lattice and coordinated water molecules. The anhydrous compound formed after dehydration is stable up to 300 °C. Subsequently, there is a distinct weight loss of 48.48% (calculated 49.56%) in the temperature range 300-590 °C, showing a DTG maximum at 492 °C, which corresponds to the decomposition of all organic moieties leading to the formation of Pr_2O_3 as the final residue above 600 °C with a remnant weight of 37.86% (calculated 38.07%).

The UV-Vis spectrum of the title compound shows absorption bands in the range 200- 330 nm (λ_{max} = 261 nm) which can be attributed to π-π* and n-π* transitions of ligand. The spectrum is shown in Supplementary data, Fig. S7. Moreover a number weak and narrow bands (characteristic of Laporte-forbidden f-f transitions of Pr^{3+} ions) are observed in the range 430–610 nm as a consequence of transitions from ground state $^3H_4$ to excited levels of 4f configuration. The main absorption band of Pr^{3+} is in the green part of the spectrum (λ_{max} = 592 nm) and corresponds to the $^3H_4 \rightarrow {}^1D_2$ transition. One less intense broad band at the blue part of the spectrum at λ_{max} = 468 nm ($^3H_4 \rightarrow {}^3P_1$) and more intense band at violet part of the spectrum at λ_{max} = 446 nm ($^3H_4 \rightarrow {}^3P_2$) are also observed[35, 36].

Magnetic susceptibility of the sample is measured at 303 K and the observed magnetic moment value, μ_{eff} is found to be 3.66 B.M. The value of μ_{eff} is close to those calculated for Pr^{3+} ions by Hund and van Vleck, which are 3.58 and 3.62 B.M. respectively[37].

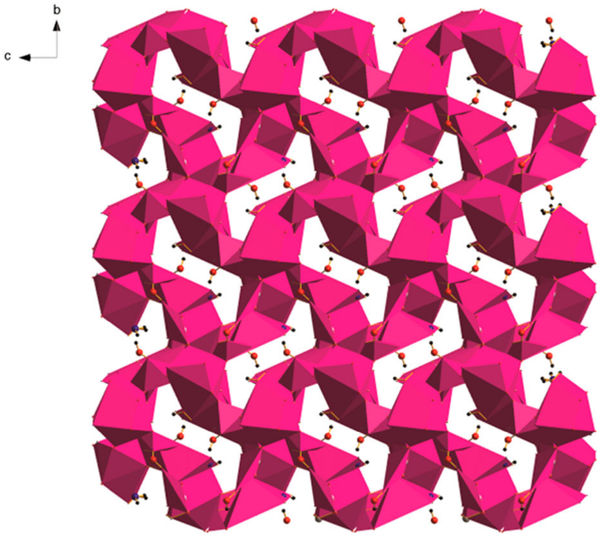

Fig. 3 — Packing diagram in polyhedral designs when viewed along ‘a’ axis.

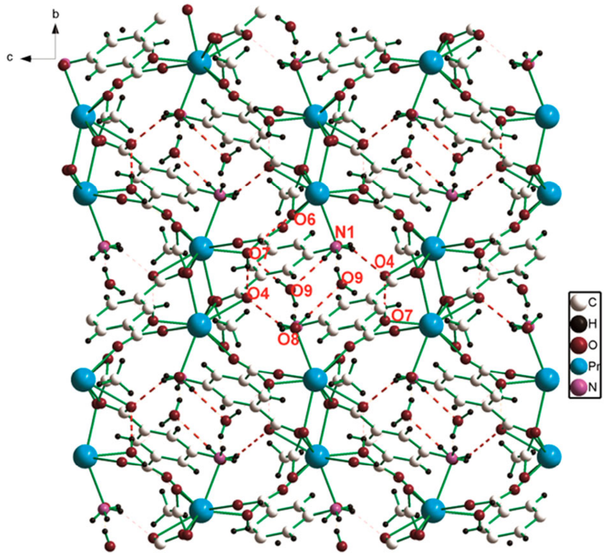

Fig. 4 — Hydrogen bonding interactions in the crystal when viewed along ‘a’ axis.

Conclusions

In summary, a new acetate bridged polymeric lanthanide complex with a composition $[Pr(CH_3COO)(AIP)(H_2O)_2]_n.nH_2O$ has been grown by single gel diffusion technique at room temperature. The functional groups present in the compound were identified by FT-IR spectral studies. UV-Vis. spectral studies show absorptions corresponding to characteristics f-f transitions of Pr^{3+} ions. The TG/DTG curves show that the compound decomposes in three stages with Pr_2O_3 as the final residue. Magnetic susceptibility studies reveal that the magnetic moment value of compound is 3.66 B.M. corresponding to two unpaired 4f electrons. The 3D polymeric framework with 'S' shaped channels offers a clear potential for gas adsorption and storage.

Supplementary data

The X-ray crystallographic data for structural analysis has been deposited in Cambridge Crystallographic Data Centre as supplementary data (CCDC no. 1857252). This can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Other supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_58A(08)886-890_SupplData.pdf.

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