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Two 3-aminobenzoates of praseodymium, $Pr(OOC\text{-}Ph\text{-}NH_2)_3(H_2O)$ and $Pr(OOC\text{-}Ph\text{-}NH_2)(OOC\text{-}Ph\text{-}NH)$

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Abstract

In the monohydrate $Pr(OOC\text{-}Ph\text{-}NH_2)_3(H_2O)$ (**1**), Pr^{3+} is nine-coordinate with only oxygen atoms coordinating. Two carboxylate groups are bidentate-bridging, four are tridentate-bridging and there is one coordinating water molecule, hence the coordination number is nine. The chains run along [0 1 0]. In the anhydrous $Pr(OOC\text{-}Ph\text{-}NH_2)(OOC\text{-}Ph\text{-}NH)$ (**2**), the central Pr^{3+} ion is surrounded by six oxygen atoms and two nitrogen atoms in a distorted square antiprism. These polyhedra are connected to each other via two opposite O–O edges to form chains running parallel [0 0 1]. The chains, in which all carboxylate groups are tridentate-bridging, are arranged in a centered rectangular fashion and are further connected via OOC-Ph-NH bridging.

Keywords: Praseodymium; 3-Amino-benzoate; Crystal structures

1. Introduction

Carboxylates and among them rare-earth carboxylates are an important and widespread class of compounds, see for a recent review [1]. In connection with our involvement with rare-earth coordination compounds in general [2], we have recently undertaken a rather systematic study on α,ω-dicarboxylates, among them glutarates, adipinates and pimelinates [3–5]. In an attempt to obtain bimetallic complexes with both hard and soft cations, for example Pr^{3+} and Hg^{2+} or Tl^+, with a bifunctional ligand such as 3-amino-benzoic acid, we have now obtained two new praseodymium 3-amino-benzoates, $Pr(OOC\text{-}Ph\text{-}NH_2)_3(H_2O)$ (**1**) and the surprising $Pr(OOC\text{-}Ph\text{-}NH_2)(OOC\text{-}Ph\text{-}NH)$ (**2**).

There are a number of rare-earth 3-amino-benzoate-trihydrates, $[M(OOC\text{-}Ph\text{-}NH_2)_3(H_2O)_3H_2O)_3$ known, M = La–Lu, Y [6] which have monomeric structures with three bidentate carboxylic ligands and three coordinating water molecules constituting a tricapped trigonal prism of oxygen atoms around M^{3+}.

2. Results and discussion

$Pr(OOC\text{-}Ph\text{-}NH_2)_3(H_2O)$ (**1**), and the isotypic $Nd(OOC\text{-}Ph\text{-}NH_2)_3(H_2O)$ as well, crystallize with an orthorhombic structure in which all Pr^{3+} are crystallographically equivalent and are nine-coordinate with only oxygen atoms coordinating, Fig. 1a. Of these, one oxygen atom originates from the water molecule of the monohydrate. Six carboxylate groups are directly attached to Pr^{3+}, two are bidentate and four monodentate. The mean Pr^{3+}–O^{2-} distance in **1** for coordination number 9 (CN 9) is 2.535 Å (see Table 1) is in excellent accord with Pr^{3+}–O^{2-} distances in similar carboxylates, for example 2.464 Å (CN 8) in $Pr(OBz)_3(HOBz)$ (HOBz = benzoic acid) [7], 2.518 Å (CN 9) in $Pr(OAc)_3(H_2O)_{1.5}$ [8] and 2.564 Å (CN 10) in $[Pr(OAc)_3(HOAc)](HOAc)$ [9]. As the formula $Pr(OOC\text{-}Ph\text{-}NH_2)_3(H_2O)$ suggests, all carboxylate groups in **1** are shared according to $Pr(OOC\text{-}Ph\text{-}NH_2)_{6/2}(H_2O)_{1/1}$ with like neighbouring coordination polyhedra, two of which are bidentate-bridging and four are tridentate-bridging, Fig. 1b. The chains run along [0 1 0], *b* is the “short” needle axis, and are packed in a way which is exhibited in Fig. 1c. There might be some additional stabilization through aromatic interaction (“π–π stacking”) [10] with phenyl groups, in the [1 0 0] direction, parallel but offset stacked although 3.81 Å apart.

$Pr(OOC\text{-}Ph\text{-}NH_2)(OOC\text{-}Ph\text{-}NH)$ (**2**) is, as far as we know, the first anhydrous rare-earth 3-amino-benzoate, and a rather

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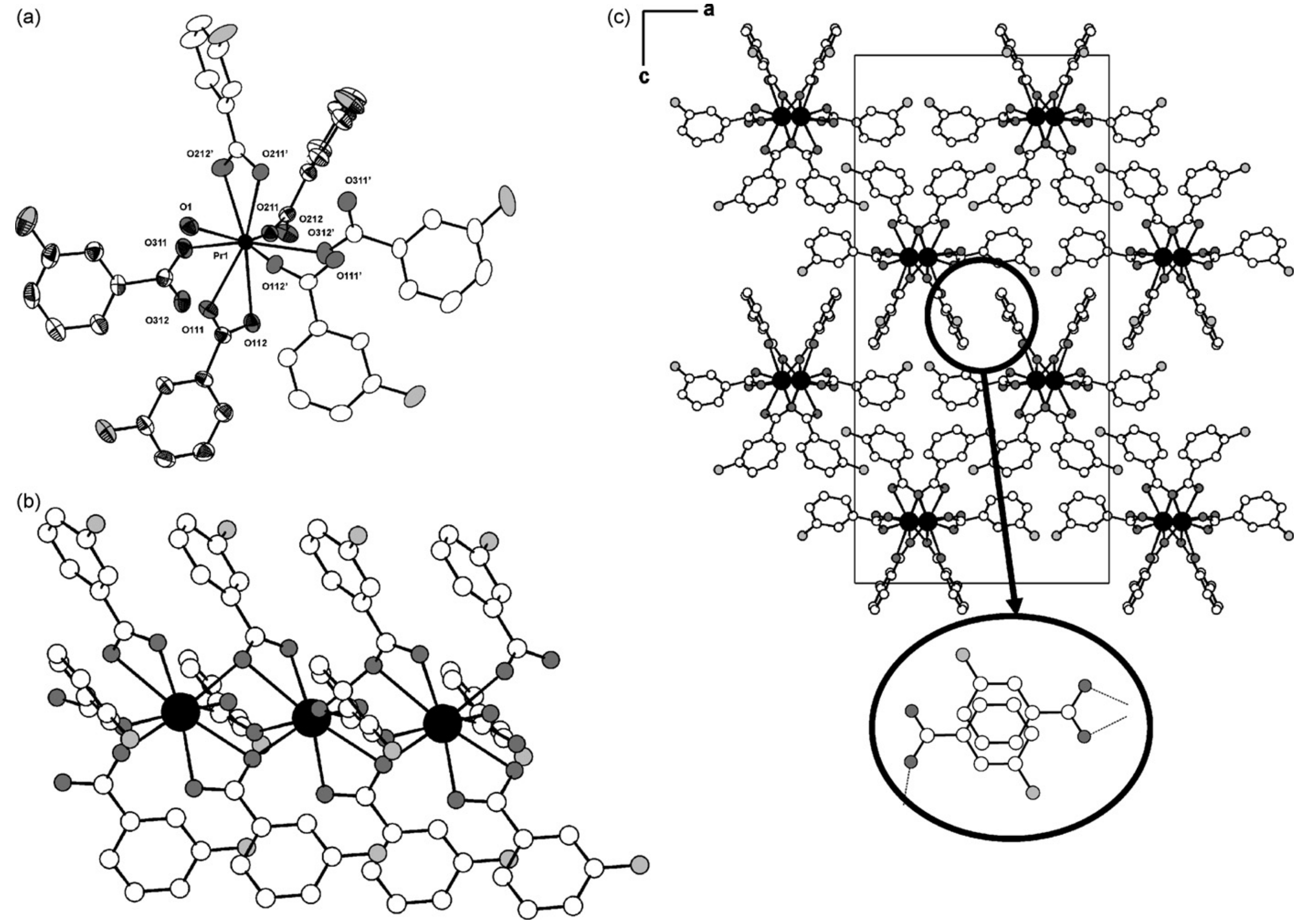

Fig. 1. (a) Details of the crystal structure of Pr(OOC-Ph-NH_2)$_3$(H_2O) (**1**) in the neighbourhood of Pr(III). Symmetry-related atoms are drawn as empty ellipsoids. (b) Part of the chains running along [0 1 0]. (c) Crystal structure viewed down the *b*-axis and, as a detail, the offset stacked phenyl groups of 3-amino-benzoic acid. The black, white, dark gray and medium gray circles symbolize Pr, C, O and N atoms.

unusual one. Under the solvothermal (ethanol) conditions with Pr_6O_{11} and $TlNO_3$ present, one of the two 3-amino-benzoic acids per formula unit is deprotonated not only at the carboxylic group but also at the amino group. As we have no indication for a lower symmetry than that of centrosymmetric space group *C*2/*c*, all amino groups are equal and, hence, we must assume that the –NH_2 and –NH groups are statistically distributed. Again, in **2** all Pr^{3+} ions are equal and are surrounded by six oxygen atoms and two nitrogen atoms as a distorted square antiprism, Fig. 2a.

Table 1
Selected interatomic distances (Å) for Pr(OOC-Ph-NH_2)$_3$(H_2O) and Pr(OOC-Ph-NH_2)(OOC-Ph-NH)

Pr(OOC-Ph-NH_2)$_3$(H_2O)		Pr(OOC-Ph-NH_2)(OOC-Ph-NH)	
Pr1–O311	2.417(3)	Pr1–O11	2.602(15) 2×
Pr1–O211	2.448(3)	Pr1–O12	2.784(5) 2×
Pr1–O111	2.459(3)	Pr1–O11′	2.878(11) 2×
Pr1–O212	2.485(4)	Pr1–N41	2.962(16) 2×
Pr1–O312	2.506(3)		
Pr1–O112	2.536(3)		
Pr1–O1	2.543(3)		
Pr1–O211′	2.601(3)		
Pr1–O112′	2.816(3)		

With an average of 2.755 Å, see Table 1, the Pr^{3+}–O^{2-} distances are much longer than in **1**. There are two additional Pr^{3+}–N^{3-} distances at 2.807 Å. The PrO_6N_2 polyhedra are connected to each other via two opposite O–O edges to chains running parallel [0 0 1], Fig. 2b. The chains, in which all carboxylate groups are tridentate-bridging, are arranged in a centered rectangular fashion and are, further, connected via OOC-Ph-NH bridging, Fig. 2c. Phenyl rings are again parallel but offset stacked and the distance between them is 3.63 Å, shorter than in **1**.

3. Experimental details

For the synthesis of Pr(OOC-Ph-NH_2)$_3$(H_2O) (**1**), a metathesis reaction of barium 3-amino-benzoate and praseodymium sulfate, molar ratio 3:1, in dry pentanol was carried out in a steel autoclave with Teflon inlay at 180 °C for 48 h and cooled to ambient temperature during 120 h. Barium 3-amino-benzoate was obtained before from a neutralisation reaction of 3-amino-benzoic acid and barium hydroxide in water. Praseodymium sulfate precipitates from an aqueous solution of praseodymium trichloride with sodium sulfate. In both cases, the precipitates were dried under vacuum for several days.

Pr(OOC-Ph-NH_2)(OOC-Ph-NH) (**2**) was obtained from the reaction of 0.15 g Pr_6O_{11}, 0.15 g $TlNO_3$ and 0.3 g 3-amino-benzoic acid in 12 ml ethanol in a steel autoclave with Teflon inlay at 140 °C for 72 h. Within one day the reac-

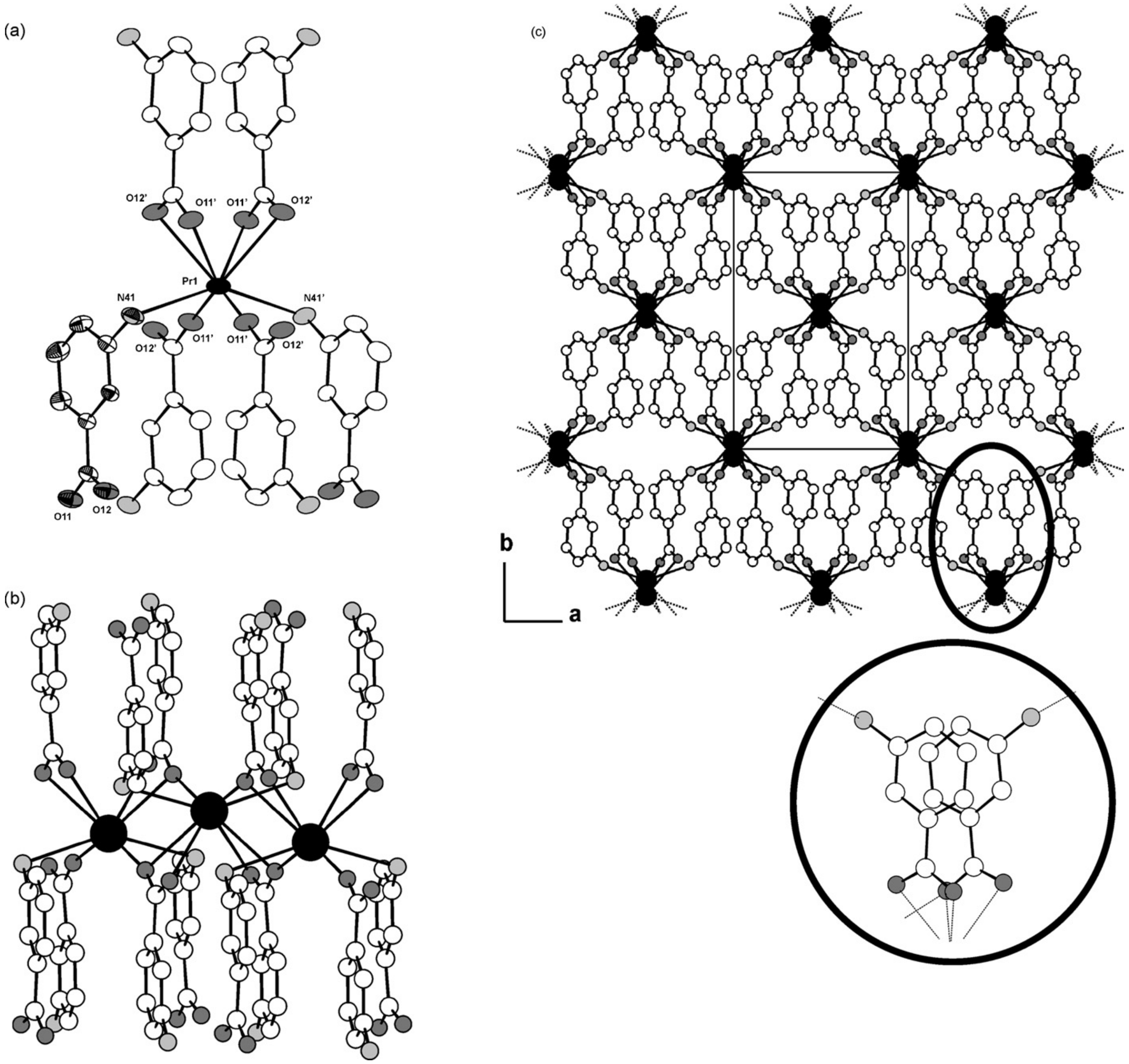

Fig. 2. (a) Details of the crystal structure of Pr(OOC-Ph-NH$_2$)(OOC-Ph-NH) (**2**) in the neighbourhood of Pr(III). Symmetry-related atoms are drawn as empty ellipsoids. (b) Part of the chains running along [0 0 1]. (c) Crystal structure of Pr(OOC-Ph-NH$_2$)(OOC-Ph-NH) viewed down the *c*-axis and, as a detail, the offset stacked phenyl groups of 3-amino-benzoic acid. The black, white, dark gray and medium gray circles symbolize Pr, C, O and N atoms.

tion mixture was cooled to 120 °C, held there for 24 h and cooled to ambient temperature within 48 h.

Suitable single crystals of both compounds, red-brown (**1**) and dark-red (**2**), were selected under a polarizing microscope and mounted in glass capillaries. Scattering intensities were collected by an imaging plate diffractometer (IPDSI/IPDSII, STOE & CIE) equipped with a normal focus, 1.75 kW, sealed tube X-ray source (Mo Kα, $\lambda = 0.71073$ Å) operating at 50 kV and 35 mA.

Intensity data for Pr(OOC-Ph-NH$_2$)$_3$(H$_2$O) (**1**) were collected at 293 K in 138 frames with ω-scans ($0 \leq \omega \leq 180°$; $\psi = 0°$, $0 \leq \omega \leq 96°$; $\psi = 90°$, $\Delta\omega = 2°$, exposure time 5 min) in the 2θ range of 1.9 to 54.8°. For the isotypic Nd(OOC-Ph-NH$_2$)$_3$(H$_2$O) see [11]. Intensity data for Pr(OOC-Ph-NH$_2$)(OOC-Ph-NH) (**2**) were collected at 293 K by ψ-scans in 100 frames ($0 \leq \psi \leq 200°$, $\Delta\psi = 2°$, exposure time 5 min) in the 2θ range of 3.8–56.3°. The data were corrected for Lorentz and polarization effects. Numerical absorption corrections based on crystal-shape optimization were applied for all data [12]. The programs used were Stoe's X-Area [13], including X-RED and X-Shape for data reduction and numerical absorption correction [14], and the WinGX suite of programs [15], including SIR-92 [16] and SHELXL-97 [17] for structure solution and refinement.

All C–H and N–H atoms were placed in idealized positions and constrained to ride on their parent atom. The H-atoms of the water molecule were located in difference Fourier maps and refined, with O–H distances restrained to 0.82(2) Å. The last cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Details of the refinements are given in Table 2.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 297928 for Pr(OOC-Ph-NH$_2$)$_3$(H$_2$O), CCDC 297927 for Pr(OOC-Ph-NH$_2$)(OOC-Ph-NH)

Table 2
Crystal data and structure refinements of Pr(OOC-Ph-NH_2)$_3$(H_2O) and Pr(OOC-Ph-NH_2)(OOC-Ph-NH)

Empirical formula	$C_{21}H_{20}N_3O_7Pr$	$C_{14}H_{11}N_2O_4Pr$
Formula weight (g mol^{-1})	567.31	412.16
Crystal system, space group	Orthorhombic, *Pbca*	Monoclinic, *C*2/*c*
Unit cell dimensions (Å/°)	$a = 15.934(2)$	$a = 10.225(2)$
	$b = 7.962(1)$	$b = 15.904(2)$
	$c = 33.086(3)$	$c = 8.562(1)$
		$\beta = 100.92(2)$
Volume (Å^3)	4197.5(7)	1367.3(4)
Z, calculated density (g/cm^3)	8, 1.795	4, 2.002
Absorption coefficient (mm^{-1})	2.371	3.580
Crystal color and habitus	Red, needle-like	Red, plate-like
Crystal size (mm^3)	0.4 × 0.1 × 0.1	0.2 × 0.2 × 0.05
Theta range for data collection (°)	1.9–54.8	3.8–56.3
Limiting indices	$-20 \leq h \leq 20$	$-13 \leq h \leq 13$
	$-9 \leq k \leq 10$	$-20 \leq k \leq 20$
	$-37 \leq l \leq 42$	$-10 \leq l \leq 10$
Reflections collected/unique	36921/2856	6381/1322
R(int)	0.0936	0.0589
Absorption correction	Numerical	Numerical
Max./min. transmission	0.7716/0.5781	0.6786/0.4511
Data/restraints/parameters	4621/2/300	1528/0/99
Goodness-of-fit on F^2	0.834	1.148
R indices[a] [$I > 2\sigma(I)$]	$R(F) = 0.0313$	$R(F) = 0.0382$
$wR_2 = 0.0607$	$wR_2 = 0.1003$	
Extinction coefficient	0.0006(1)	0.009(1)
Largest difference peak/hole (e Å^{-3})	0.97 (1.39 Å from Pr1) −0.85 (0.81 Å from Pr1)	1.15 (0.42 Å from C6) −1.42 (0.85 Å from Pr1)

[a] $R1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$, $wR2 = [\Sigma w(|F_o|2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2}$, $S_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n-p)]^{1/2}$, with $w = 1/[\sigma^2(|F_o|^2) + (0,0346\,P)^2]$ for Pr(OOC-Ph-NH_2)$_3$(H_2O) and $w = 1/[\sigma^2(|F_o|^2) + (0,0792 \cdot P)^2]$ for Pr(OOC-Ph-NH_2)(OOC-Ph-NH), were $P = (|F_o|^2 + 2|F_c|^2)/3$. $F_c{}^* = k\,F_c\,[1 + 0{,}001 \cdot |F_c|^2\,\lambda^3/\sin(2\theta)]^{-1/4}$.

and CCDC 297935 for Nd(OOC-Ph-NH_2)$_3$(H_2O). Copies of the data can be obtained, free of charge, on application to CHGC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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[11] Nd(OOC-Ph-NH2)3(H2O): C21H20N3O7Nd (570.64 g.mol−1); diffractometer IPDS-I, Stoe, Darmstadt; Mo Kα (graphite monochromator, $\lambda = 0.71073$ Å); $T = 293(2)$ K; $\theta_{max} = 28.14°$; 100 images, $0° \leq \varphi \leq 200°$; $\Delta\varphi = 2°$; indices: $-21 \leq h \leq 21$, $-9 \leq k \leq 9$, $-43 \leq 1 \leq 43$; $\rho_{calc} = 1.798$ g cm^{-3}; 23231 reflection intensities measured of which 2686 were symmetrically independent, $R_{int} = 0.1045$, $F(000) = 2264$, $\mu = 2.512$ mm^{-1}. Orthorhombic, *Pbca* (no. 61), a = 15.937(2), $b = 7.970(1)$, $c = 33.194(6)$ Å, $V = 4216.5(10)$ Å3, $Z = 8$. *R* values: $R1/wR2$ for 4779 reflections with $[I_0 > 2\sigma(I_0)]$: 0.0457/0.0972 and for all data: 0.1027/0.1151; $S_{all} = 0.896$.

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