

A lanthanum(III) complex with a lacunary polyoxotungstate: $\text{Na}_2(\text{NH}_4)_7[\text{La}(\text{W}_5\text{O}_{18})_2] \cdot 16\text{H}_2\text{O}$ Filipe A. Almeida Paz,^{a*}
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Key indicators

Single-crystal X-ray study
 $T = 100 \text{ K}$
Mean $\sigma(\text{La}-\text{O}) = 0.006 \text{ \AA}$
H-atom completeness 0%
 R factor = 0.031
 wR factor = 0.081
Data-to-parameter ratio = 15.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of a lanthanum polyoxotungstate complex, *viz.* heptaammonium disodium decatungstolanthanate hexadecahydrate, $\text{Na}_2(\text{NH}_4)_7[\text{La}(\text{W}_5\text{O}_{18})_2] \cdot 16\text{H}_2\text{O}$, has been determined by single-crystal X-ray diffraction at 100 (2) K in the space group $C2/c$. The $[\text{La}(\text{W}_5\text{O}_{18})_2]^{9-}$ polyoxoanion has the central La^{3+} cation located on a twofold rotation axis. The close packing of the polyoxoanion-supported lanthanum(III) complexes with Na^+ and NH_4^+ cations leads to the formation of several intersecting undulating channels, where the water molecules of crystallization are located and involved in strong hydrogen bonds.

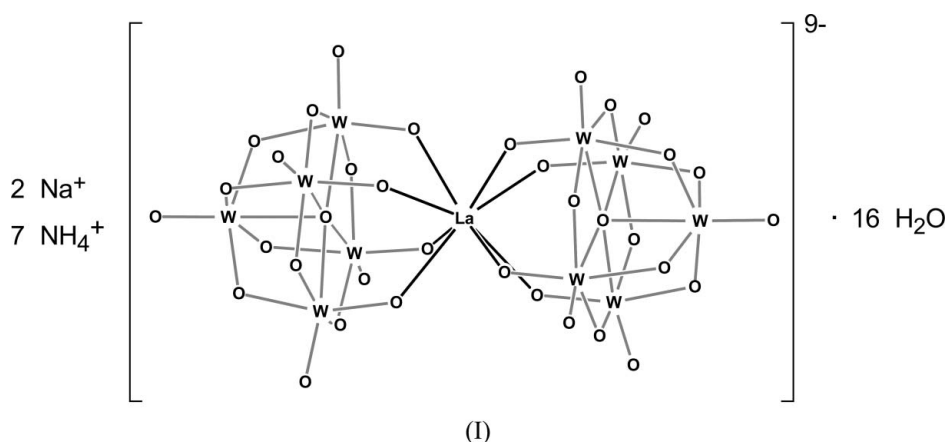
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Comment

Polyoxometalates (POMs) are a unique type of compound showing remarkable structural diversity and potentially interesting applications in catalysis, non-linear optical and magnetic materials, liquid crystals and biomedical materials (Pope & Müller, 1994, 2001; Müller *et al.*, 1998, and references therein; Pope, 1983). In the course of our research on the synthesis and structural characterization of novel functional materials containing POMs (Almeida Paz *et al.*, 2004; Sousa, Paz, Cavaleiro *et al.*, 2004; Sousa, Paz, Soares-Santos *et al.*, 2004), we came across the title compound, (I).



A search in the literature and in the Inorganic Crystal Structure Database (Belsky *et al.*, 2002) shows that the $[\text{La}(\text{W}_5\text{O}_{18})_2]^{9-}$ polyoxoanion shares striking similarities with all complexes of the $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{n-}$ type, where $\text{Ln} = \text{Ce}^{4+}$ (Peacock & Weakley, 1971; Iball *et al.*, 1974), Ce^{3+} (Xue *et al.*, 2002), Pr^{3+} , Nd^{3+} (Ozeki & Yamase, 1994*a*), Sm^{3+} (Ozeki & Yamase, 1993, 1994*a,b*), Eu^{3+} (Sugeta & Yamase, 1993; Yamase *et al.*, 1993), Gd^{3+} (Yamase & Ozeki, 1993; Ozeki & Yamase, 1994*a*; Yamase *et al.*, 1994), Tb^{3+} (Ozeki & Yamase, 1994*a*; Ozeki *et al.*, 1992), Dy^{3+} (Ozeki & Yamase, 1994*a*) and

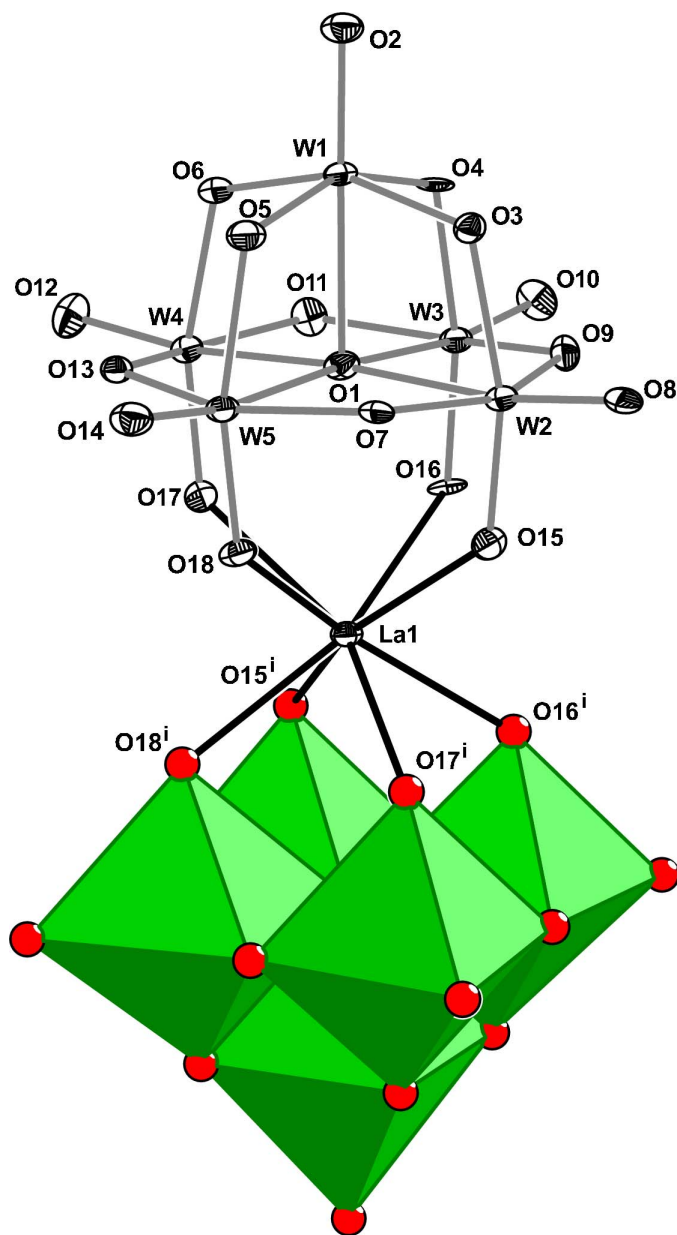


Figure 1

Mixed ellipsoid and polyhedral representation of the polyoxoanion-supported lanthanum(III) complex anion, $[\text{La}(\text{W}_5\text{O}_{18})_2]^{9-}$, showing the labelling scheme for selected atoms and emphasizing the square antiprismatic coordination environment for the central La^{3+} cation. Atoms belonging to the asymmetric unit are represented with ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $2 - x, y, \frac{3}{2} - z$].

also with the actinide cation Th^{4+} (Griffith *et al.*, 2000). Surprisingly, the structure containing La^{3+} cations has not been reported to date. We describe here the synthesis and crystal structure of $\text{Na}_2(\text{NH}_4)_7[\text{La}(\text{W}_5\text{O}_{18})_2] \cdot 16\text{H}_2\text{O}$, determined in the space group $C2/c$ at the low temperature of 100 (2) K; this is also the first report of a complex of the $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{n-}$ type crystallizing with NH_4^+ cations.

The $[\text{La}(\text{W}_5\text{O}_{18})_2]^{9-}$ polyoxoanion has crystallographic C_2 symmetry about an axis passing through the central La^{3+} cation and perpendicular to the vector containing the W1 , La1 and W1^i centres [Fig. 1; symmetry code: (i) $2 - x, y, \frac{3}{2} - z$]. The

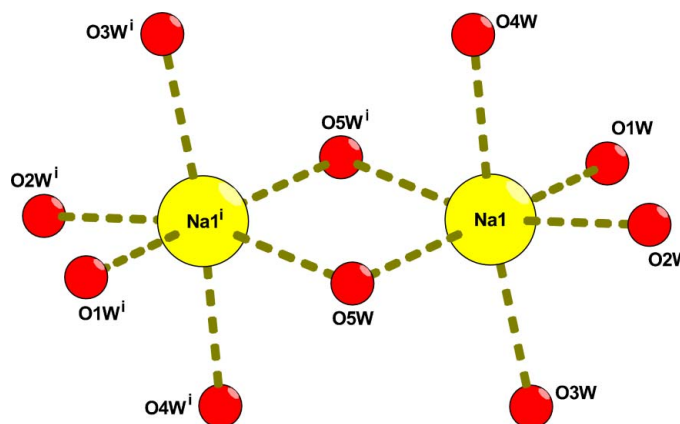


Figure 2

Schematic representation of the cationic $\{\text{Na}_2(\text{H}_2\text{O})_{10}\}^{2+}$ moieties. The $\text{Na1} \cdots \text{Na1}^i$ distance is 3.411 (7) Å [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$].

two $[\text{W}_5\text{O}_{18}]^{6-}$ anionic fragments are linked together *via* a central La^{3+} cation positioned in the lacuna of each anion (Fig. 1). This centre exhibits typical square antiprismatic coordination geometry, with $\text{La}-\text{O}$ distances in the range 2.497 (6)–2.562 (6) Å (Table 1 and Fig. 1). The degree of staggering between the upper and lower square faces of the antiprism is only *ca* 0.6° from ideal.

For the $[\text{W}_5\text{O}_{18}]^{6-}$ moieties, the five crystallographically unique W centres exhibit distorted $\{\text{WO}_6\}$ octahedral environments, in which the central W atom is displaced in the direction of the axial oxo ligand (average distance of displacement = 0.402 Å): $\text{W}-\text{O}$ distances and $\text{O}-\text{W}-\text{O}$ angles are in the ranges 1.724 (6)–2.324 (6) Å and 74.5 (2)–179.0 (3)° [74.5 (2)–104.3 (3)° and 153.2 (2)–179.0 (3)° for *cis* and *trans*], respectively. The $\text{W}-\text{O}$ distances can be divided into several groups according to the different types of O atoms (Table 3): O_I represent long bonds of the $\text{W}-\text{O1}-\text{W}$ type (where O1 is the core O atom; see Fig. 1) found in the range 2.304 (6)–2.324 (6) Å; O_{II} represent those connected to the W centres which are involved in edge-sharing of adjacent octahedra [1.890 (6)–2.031 (6) Å]; O_{III} represent the lanthanum-bound O atoms (O15, O16, O17 and O18), and O_{IV} the terminal O atoms (O2, O8, O10, O12 and O14; see Fig. 1 and Table 3). As found in related compounds, pairs of short and long $\text{W}-\text{O}_{II}$ bonds are observed (Table 3). This results from small displacements of the W centres, and also from the structural evidence that W1 is the statistically farthest W centre from any other: the $\text{W} \cdots \text{W}$ distances for the $\text{W2} \cdots \text{W3} \cdots \text{W4} \cdots \text{W5}$ central square of $[\text{W}_5\text{O}_{18}]^{6-}$ are in the range 3.264 (6)–3.291 (6) Å, while $\text{W1} \cdots \text{W2}-\text{W5}$ distances are in the range 3.331 (6)–3.342 (6) Å. It is interesting to note that the O1 core atom lies only 0.099 (6) Å out of the plane of the equatorially bonded $\text{W2}-\text{W5}$ centres and in the direction of W1; the non-bonded $\text{La1} \cdots \text{O1}$ distance is 3.271 (6) Å.

The anion charge is balanced by the presence of one Na^+ and three and a half crystallographically unique NH_4^+ cations, $\text{Na}_2(\text{NH}_4)_7[\text{La}(\text{W}_5\text{O}_{18})_2]$. Interestingly, the Na^+ cations in the crystal structure form $\{\text{Na}_2(\text{H}_2\text{O})_{10}\}^{2+}$ moieties, exhibiting a highly distorted octahedral coordination environment in

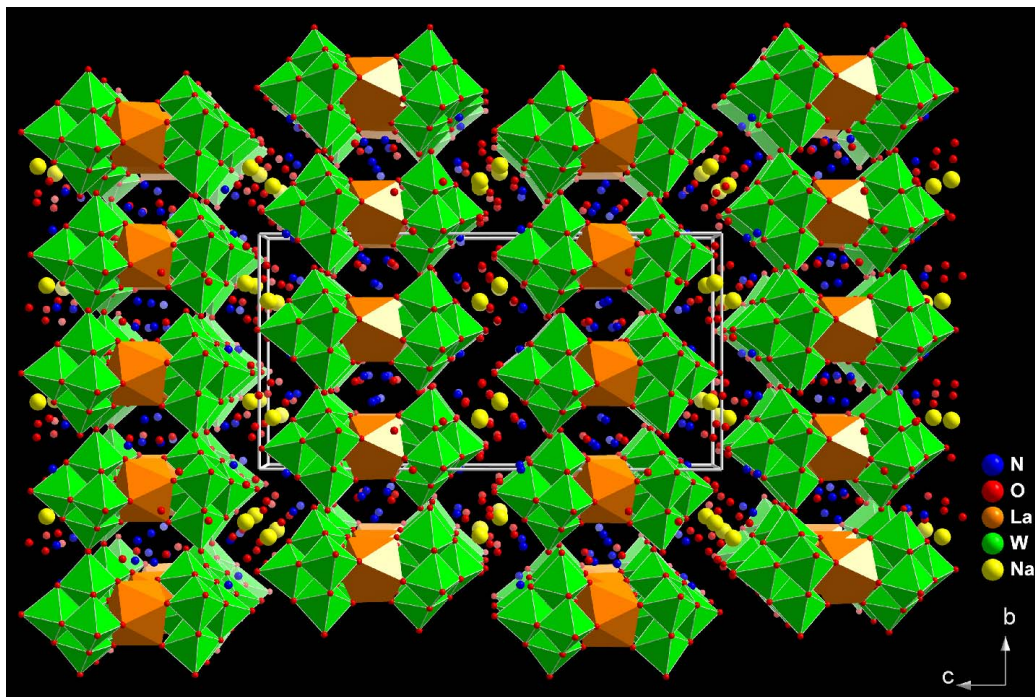


Figure 3
Polyhedral representation of the crystal packing of $\text{Na}_2(\text{NH}_4)_7[\text{La}(\text{W}_5\text{O}_{18})_2] \cdot 16\text{H}_2\text{O}$, viewed along the a direction.

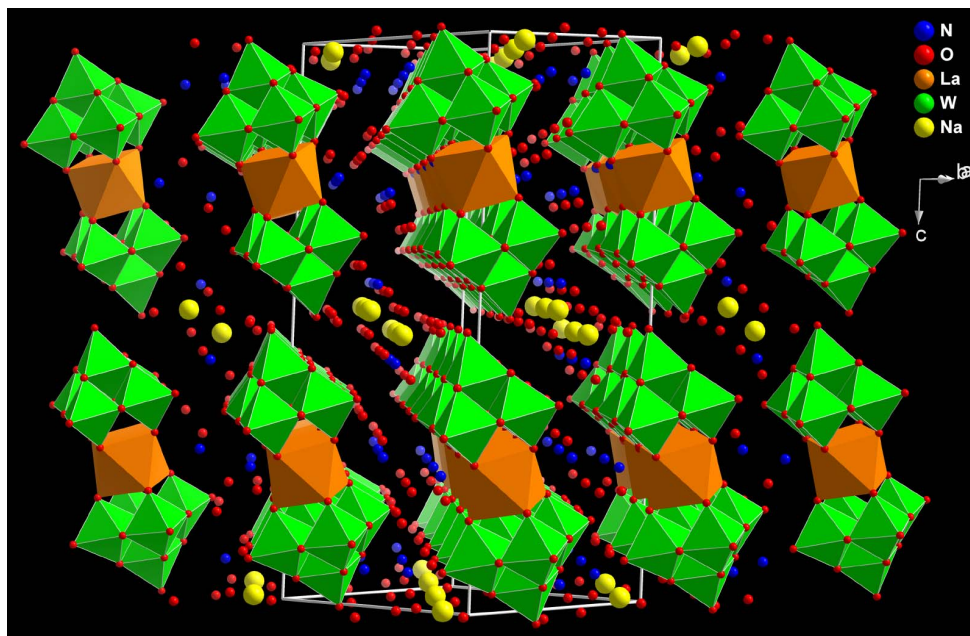


Figure 4
Polyhedral representation of the crystal packing of $\text{Na}_2(\text{NH}_4)_7[\text{La}(\text{W}_5\text{O}_{18})_2] \cdot 16\text{H}_2\text{O}$, viewed towards the $(\bar{8},11,1)$ plane.

which the average $\text{Na} \cdots \text{O}_{\text{water}}$ contact distance is 2.372 Å (Table 2 and Fig. 2) and the $\text{Na}1^{\text{ii}} \cdots \text{Na}1^{\text{ii}}$ distance is 3.411 (7) Å [symmetry code: (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$].

The polyoxoanion-supported lanthanum(III) complex anions, $[\text{La}(\text{W}_5\text{O}_{18})_2]^{9-}$, pack closely in the ab plane in a typical brick-wall-like fashion, leading to several types of intersecting channels which accommodate the cations (Na^+ and NH_4^+) and the water molecules of crystallization (Figs. 3

and 4). These are, in turn, involved in an extensive hydrogen-bonded network composed of strong heteronuclear $\text{N}^+ \cdots \text{H} \cdots \text{O}$ and homonuclear $\text{O} \cdots \text{H} \cdots \text{O}$ interactions (not shown).

Experimental

All chemicals were purchased from Aldrich and used without further purification. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (9.90 g, 30 mmol) and H_3BO_3 (0.15 g, 2.43 mmol) were dissolved in hot distilled water (*ca* 21 ml, 363–

373 K), and the final pH was adjusted to 7.1 using a 6 M aqueous solution in HCl. After 10 min, a solution of La(NO₃)₃ (3.24 mmol) in 1 M CH₃COOH (ca 5.4 ml) was added dropwise, and the resulting mixture was stirred thoroughly at 363 K for 30 min. The temperature was then slowly dropped to 343 K, after which an aqueous solution of NH₄Cl (12 g, 224 mmol) was added dropwise. The resulting solution was allowed to stand at ambient temperature for 24 h and then filtered. The collected solid was recrystallized from warm distilled water, giving good quality white crystals suitable for X-ray diffraction. Selected FT-IR data (cm⁻¹): ν(N⁺-H, from NH₄⁺) = 1401 (s), ν_{as}(W-O_{IV}, terminal W-O stretch) = 931 (s), ν_{as}(W-O_{II}-W, edge-shared W-O-W stretching mode) = 840 (s) and 789 (s).

Crystal data

Na ₂ (NH ₄) ₇ [La(W ₅ O ₁₈) ₂].16H ₂ O	$D_x = 3.935 \text{ Mg m}^{-3}$
$M_r = 3013.94$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 1014 reflections
$a = 11.784 (2) \text{ \AA}$	$\theta = 2.7\text{--}28.7^\circ$
$b = 14.838 (3) \text{ \AA}$	$\mu = 23.47 \text{ mm}^{-1}$
$c = 29.143 (6) \text{ \AA}$	$T = 100 (2) \text{ K}$
$\beta = 93.26 (3)^\circ$	Plate, white
$V = 5087.4 (18) \text{ \AA}^3$	$0.35 \times 0.21 \times 0.06 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART CCD1000 diffractometer	5183 independent reflections
Thin-slice ω and φ scans	4577 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	$R_{\text{int}} = 0.069$
$T_{\text{min}} = 0.045$, $T_{\text{max}} = 0.333$	$\theta_{\text{max}} = 26.4^\circ$
21 307 measured reflections	$h = -14 \rightarrow 14$
	$k = -18 \rightarrow 18$
	$l = -36 \rightarrow 36$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0169P)^2 + 65.9468P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.081$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.08$	$\Delta\rho_{\text{max}} = 1.66 \text{ e \AA}^{-3}$
5183 reflections	$\Delta\rho_{\text{min}} = -2.16 \text{ e \AA}^{-3}$
326 parameters	
H-atom parameters not defined	

Table 1

Selected geometric parameters (\AA , $^\circ$).

La1-O15	2.497 (6)	La1-O16	2.530 (6)
La1-O18	2.511 (6)	La1-O17	2.562 (6)
O15-La1-O15 ⁱ	151.4 (3)	O16 ⁱ -La1-O16	75.0 (3)
O15-La1-O18	72.7 (2)	O15-La1-O17	112.8 (2)
O15-La1-O18 ⁱ	133.7 (2)	O15 ⁱ -La1-O17	74.8 (2)
O18-La1-O18 ⁱ	74.3 (3)	O18-La1-O17	70.99 (19)
O15-La1-O16 ⁱ	84.66 (19)	O18 ⁱ -La1-O17	85.41 (19)
O18-La1-O16 ⁱ	151.71 (19)	O16 ⁱ -La1-O17	135.25 (19)
O15-La1-O16	72.61 (19)	O16-La1-O17	72.16 (19)
O15 ⁱ -La1-O16	84.7 (2)	O15-La1-O17 ⁱ	74.8 (2)
O18-La1-O16	112.58 (19)	O17-La1-O17 ⁱ	150.5 (3)

Symmetry code: (i) $2 - x, y, \frac{3}{2} - z$.

Table 2

Contact distances (\AA).

Na1...O1W	2.346 (8)	Na1...O4W	2.328 (7)
Na1...O2W	2.402 (7)	Na1...O5W	2.379 (8)
Na1...O3W	2.321 (7)	Na1 ⁱⁱ ...O5W	2.456 (7)

Symmetry code: (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

Table 3

W-O bond-distance categories (\AA) for the [W₅O₁₈]⁶⁻ anionic fragment present in (I).

Category	Range	Average	Range
W-O _I	2.304 (6)–2.324 (6)	2.314	0.020
W-O _{II} (short)	1.890 (6)–1.963 (6)	1.927	0.073
W-O _{II} (long)	2.022 (6)–2.031 (6)	2.027	0.009
W-O _{III}	1.776 (6)–1.790 (6)	1.783	0.014
W-O _{IV}	1.726 (6)–1.734 (6)	1.730	0.008

The distinction between water molecules and NH₄⁺ cations proved to be very difficult. In order to balance the anion charge, three and a half NH₄⁺ cations have been selected, taking into consideration FT-IR data and geometrical aspects, such as charge proximity and the number of neighbours with which hydrogen bonding might occur. Since the number of possible hydrogen bonds in which the water molecules and NH₄⁺ cations could be involved is quite large, no attempt was made either to find or to place geometrically the H atoms in these groups. The highest peak in the final difference Fourier map was located 1.25 \AA from O4 and the deepest hole 0.94 \AA from W1.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve and refine structure: SHELXTL (Bruker, 2001); molecular graphics: DIAMOND (Brandenburg, 2001); software used to prepare material for publication: SHELXTL.

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