

A Chain-like Polyoxotungstate Constructed from $[\text{CeW}_{10}\text{O}_{36}]^{9-}$, $[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}]^{4+}$, and $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$ Units: $(\text{NH}_4)_3[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}]\{[\text{Na}(\text{H}_2\text{O})_4]_2[\text{CeW}_{10}\text{O}_{36}]\} \cdot 6 \text{H}_2\text{O}$

Ling Yuan^{a,b}, Chao Qin^a, Xinlong Wang^a, and Enbo Wang^a

^a Key Laboratory of Polyoxometalate Science of the Ministry of Education, Institute of Polyoxometalate Chemistry, Department of Chemistry, Northeast Normal University, Changchun Jilin 130024, People's Republic of China

^b Department of Chemistry, Xingan Occupation Technic College Wulanhaote, 137400, People's Republic of China

Reprint requests to Prof. Enbo Wang. E-mail: wangenbo@public.cc.jl.cn or wangeb889@nenu.edu.cn

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An unusual cerium-containing decaoxotungstate complex, $(\text{NH}_4)_3[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}]\{[\text{Na}(\text{H}_2\text{O})_4]_2[\text{CeW}_{10}\text{O}_{36}]\} \cdot 6\text{H}_2\text{O}$ (**1**) has been synthesized and characterized by IR, TG, and single crystal X-ray diffraction studies (yellow crystals, orthorhombic, space group *Imm2*, $a = 11.473(2)$, $b = 15.225(3)$, $c = 17.646(7)$ Å, $V = 3082.3(15)$ Å³, $Z = 2$, $R = 0.046$). In this compound, sandwich-type $[\text{CeW}_{10}\text{O}_{36}]^{9-}$ clusters are linked by binuclear $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$ units by sharing oxygen atoms into linear chains, which are further extended into a 2D supramolecular network *via* pentanuclear $[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}]^{4+}$ units by strong hydrogen bonding interactions.

Key words: Polyoxotungstate, Cerium, Cluster, Crystal Structure

Introduction

Polyoxometalates (POMs), as early transition metal oxide clusters, show unusual properties and a variety of compositions and structures that make them attractive for applications in catalysis, separation, imaging, materials science, and medicine [1–3]. The extension of discrete POM subunits by using various kinds of linkages into one-, two- and three-dimensional networks continues to be a focus of considerable ongoing research not only from a structural point of view, but also because the as-synthesized materials may possess novel properties owing to synergistic effects. Up to now, classic Keggin- [4–8], Wells-Dawson- [9], Silvertown- [10], Lindqvist- [11], and Anderson-type polyoxoanion clusters [12] have been successfully used as building blocks for the construction of extended inorganic aggregates. For example, Zubietta *et al.* employed transition metal ion complexes as inorganic bridging ligands linking hexa-molybdate clusters into a two-dimensional network [11]. Sécheresse's group prepared several 1D and 2D frameworks with ϵ -Keggin polyoxometalates through the linking of organic groups [5], while Lu's

group isolated a novel three-dimensional framework formed by $[\text{GdMo}_{12}\text{O}_{42}]^{9-}$ anions and rare earth cations [10], and recently our group has reported a series of extended architectures assembled from Anderson-type polyoxoanions [13].

Among the reported POM clusters, lanthanide-containing POM anions are the focus of research due to their antiviral and anti-HIV properties as well as their excellent photoluminescence behavior. The $[\text{LnW}_{10}\text{O}_{36}]^{9-}$ polyoxoanions, where $\text{Ln} = \text{La}^{3+}$ [14], Ce^{3+} [15a], Pr^{3+} [16], Nd^{3+} [16], Sm^{3+} [16–18], Eu^{3+} [19–21], Gd^{3+} [16, 22], Tb^{3+} [16, 23], and Dy^{3+} [16] have been isolated as discrete clusters, however, examples for utilizing them for the design and synthesis of POMs with extended structures have never been reported. As a continuation of work on various POM derivatives, we are trying to construct novel extended structures based on the $[\text{CeW}_{10}\text{O}_{36}]^{9-}$ anion. Herein, we report the synthesis, characterization and crystal structure of a new polyoxotungstate complex $(\text{NH}_4)_3[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}]\{[\text{Na}(\text{H}_2\text{O})_4]_2[\text{CeW}_{10}\text{O}_{36}]\} \cdot 6 \text{H}_2\text{O}$ (**1**) which exhibits a linear chain based on $[\text{CeW}_{10}\text{O}_{36}]^{9-}$ polyoxoanions and binuclear $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$ units. These chains are further con-

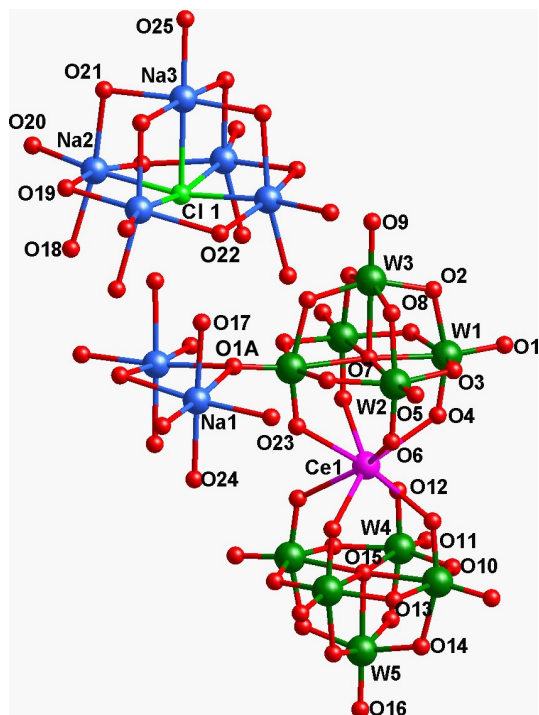


Fig. 1. ORTEP drawing of the fundamental building blocks of **1**, highlighting the three types of metal-oxygen units.

nected by pentanuclear $[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}]^{4+}$ units into a 2D supramolecular framework *via* extensive hydrogen-bonds. To our knowledge, compound **1** represents the first extended structure composed of the $[\text{CeW}_{10}\text{O}_{36}]^{9-}$ polyoxoanion since it was first isolated by Weakley in 1971 [15b].

Results and Discussion

Structure description

Single crystal X-ray diffraction analysis has revealed that compound **1** contains three types of metal-oxygen clusters: a sandwich-type $[\text{CeW}_{10}\text{O}_{36}]^{9-}$ polyoxoanion, the binuclear $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$ unit, and a pentanuclear $[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}]^{4+}$ unit. The sandwich-type polyoxoanion, as shown in Fig. 1, consists of two $[\text{W}_5\text{O}_{18}]^{6-}$ moieties and a central Ce^{3+} cation fixed in the cavity of each anion *via* W–O–Ce connecting modes. Each $[\text{W}_5\text{O}_{18}]^{6-}$ subunit is made up of five edge-sharing $\{\text{WO}_6\}$ octahedra (Fig. 2). The W–O bonds can be divided into three groups, *i.e.* W–O(t) bonds, W–O(μ_2) bonds, and W–O(μ_5) bonds, whose bond lengths fall in the ranges 1.716(11)–1.742(12), 1.750(17)–2.034(14), and 2.29(3)–2.324(2) Å, re-

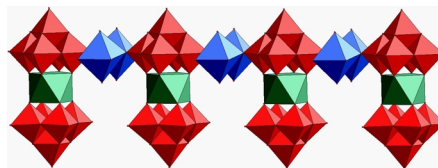


Fig. 2. A polyhedral representation of the one-dimensional chain in **1**.

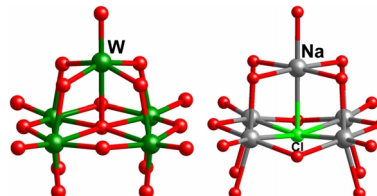


Fig. 3. The ball-and-stick representations of $[\text{W}_5\text{O}_{18}]^{6-}$ (left) and $[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}]^{4+}$ (right) units.

spectively. These values are comparable to those of other isomorphous $[\text{LnW}_{10}\text{O}_{36}]^{9-}$ anions. The coordination polyhedron around the central Ce^{3+} cation can be described as a square antiprism. The Ce–O bond lengths are in the range of 2.489(17)–2.499(15) Å and the O–Ce–O bond angles range from 73.4(3) to 142.4(3)°. It is interesting that these sandwich-type polyoxoanions are not isolated but linked together through binuclear $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$ units into a 1D chain along the *a* axis (Fig. 2) by sharing two terminal oxygen atoms (O1 and O1A) at opposite sides of each polyoxoanion. For each binuclear $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$ unit, the Na^+ cations adopt distorted octahedral coordination environments and the non-bonding $\text{Na}\cdots\text{Na}$ distance is 3.536(15) Å. The Na–O_{POM} bond length is 2.474(12) Å. The residual coordination sites of each sodium ion are occupied by water molecules. The distances Na–O_w vary from 2.33(3) to 2.39(3) Å. The bond valence sum (BVS) calculations [26] for O(17), O(23), O(24) give the values 0.782, 0.784 and 0.802, respectively, indicating that they are diprotonated oxygen atoms in view of the bond valence contribution of ~ 0.8 for an O–H bond. It is noteworthy that the composition of the $[\text{Na}_2(\text{H}_2\text{O})_8\text{O}_2]$ unit in **1** is different from that of $[\text{Na}_2(\text{H}_2\text{O})_{10}]^{2+}$ contained in a previously reported compound $\text{Na}_2(\text{NH}_4)_7[\text{La}(\text{W}_5\text{O}_{18})_2] \cdot 16\text{H}_2\text{O}$ [14] in that all the oxygen atoms bonded to the Na^+ cations of $[\text{Na}_2(\text{H}_2\text{O})_{10}]^{2+}$ come from water molecules. This distinction results in the $[\text{LaW}_{10}\text{O}_{36}]^{9-}$ anions being isolated rather than being linked into chains as in **1**.

Interestingly, apart from the binuclear $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$ unit, a new type of pentanuclear $[\text{Na}_5$

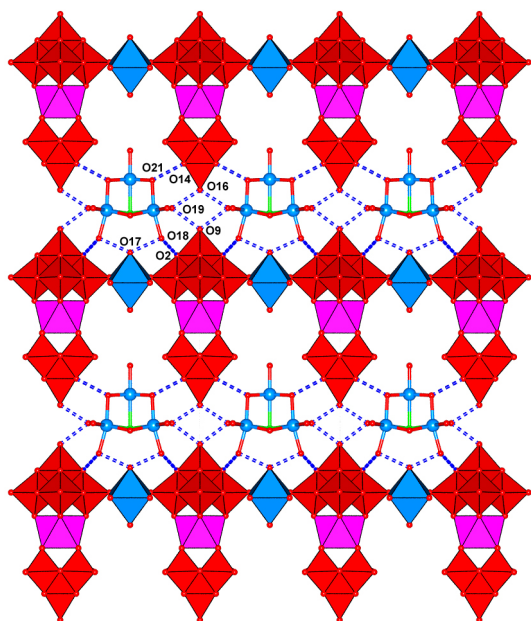


Fig. 4. The 2D layered framework of **1** formed by the extensive hydrogen bonds among $[\text{CeW}_{10}\text{O}_{36}]^{9-}$, $[\text{Na}_2(\text{H}_2\text{O})_{10}]^{2+}$, and $[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}]^{4+}$. NH_4^+ ions were omitted for clarity.

$(\text{H}_2\text{O})_{17}\text{Cl}]^{4+}$ aggregate is found in the crystal. As illustrated in Fig. 3, the linking mode of the pentanuclear $[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}]^{4+}$ unit is identical with that of the $[\text{W}_5\text{O}_{18}]^{6-}$ subunit, *i. e.* five $\{\text{NaO}_5\text{Cl}\}$ octahedra are joined together in an edge-sharing mode with Na–O distances of 2.377(17)–2.484(17) Å and Na–Cl distances of 2.745(7)–2.824(18) Å. We therefore guess that $[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}]^{4+}$ units may also form a sandwich-type structure $[\text{Ln}(\text{Na}_5\text{O}_{17}\text{Cl})_2]^{n-}$ because the surface oxygen atoms have the ability to capture metal ions. The bond valence sum (BVS) calculations for O(18), O(19), O(20), O(21), O(22), and O(25) give values of 0.786, 0.759, 0.770, 0.769, 0.761, and 0.795, respectively, suggesting that they are diprotonated oxygen atoms. The pentanuclear $[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}]^{4+}$ units link the 1D chains into a 2D supramolecular network *via* extensive hydrogen bonds [O(21)···O(14) 2.968(4) Å, O(19)···O(16) 2.742(3) Å, O(19)···O(9) 2.870(3) Å, O(18)···O(2) 2.776(3) Å, O(18)···O(17) 2.810(3) Å] (Fig. 4).

IR spectroscopy

In the IR spectrum of compound **1**, the peaks at 943, 839, 783 and 702 cm^{-1} can be attributed to $\nu(\text{W}-\text{O}_i)$, $\nu(\text{W}-\text{O}_b)$ and $\nu(\text{W}-\text{O}_c)$ of the polyoxoanion skeleton.

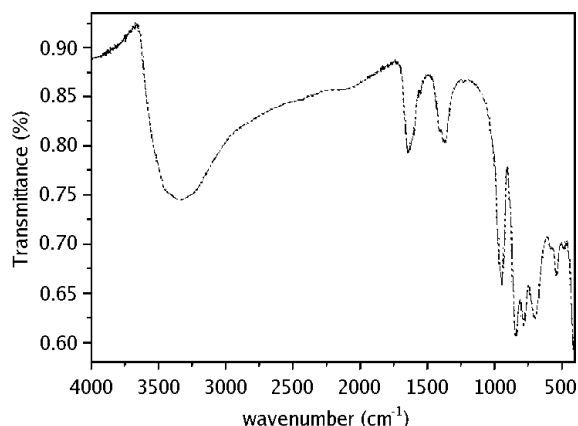


Fig. 5. IR spectrum of compound **1**.

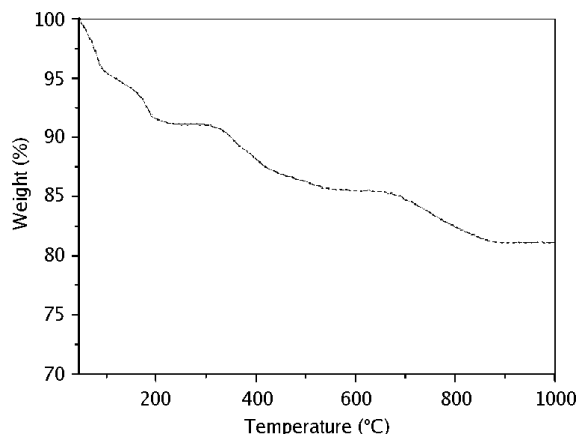


Fig. 6. TGA curve of compound **1**.

The broad band at *ca.* 3366 cm^{-1} is attributed to the vibration of the water ligand (Fig. 5).

Thermal analysis

The result of the TG analysis basically agrees with that of the structure determination (Fig. 6). The first step (4.30 %) in the temperature range 70–98 °C corresponds to the release of all lattice water and ammonia molecules (4.22 %). The second step (4.39 %) in the temperature range of 98–230 °C corresponds to the loss of the coordinated water molecules of the $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$ unit (4.28 %). The weight loss of 9.86 % in the range 300–880 °C corresponds to the demolishing of the $[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}]^{4+}$ units (10.18 %). Above 880 °C, no further weight loss was found.

Conclusion

In summary, we have synthesized and crystallized a new compound $(\text{NH}_4)_3[\text{Na}_5(\text{H}_2\text{O})_{17}\text{Cl}][\{\text{Na}(\text{H}_2\text{O})_4\}_2-$

Table 1. Crystal data and structure refinements for compound **1**.

Empirical formula	H ₇₀ CeClN ₃ Na ₇ O ₆₇ W ₁₀
Formula weight	3359.59
Temperature, K	293
Wavelength, Å	0.71073
Crystal system	orthorhombic
space group	<i>Imm2</i>
<i>a</i> , Å	11.473(2)
<i>b</i> , Å	15.225(3)
<i>c</i> , Å	17.646(7)
Volume, Å ³	3082.3(15)
<i>Z</i>	2
<i>d</i> _{calc} , g cm ^{−3}	3.62
Absorption coefficient, mm ^{−1}	19.5
<i>F</i> (000), e	3038
Crystal size, mm ³	0.31 × 0.26 × 0.23
θ range, deg.	3.21–24.99
Limiting indices <i>hkl</i>	±13, ±18, ±20
Reflections collected	12102
Independent reflections	2942
Transmission max/min	0.0940.065
Data/restraints/parameters	2942/1/244
Goodness-of-fit on <i>F</i> ²	1.018
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.046/0.091
<i>R</i> ₁ / <i>wR</i> ₂ (all data) ^{a,b}	0.049/0.092
<i>x</i> Parameter (Flack)	0.00(2)
Largest diff. peak/hole, e Å ^{−3}	1.41/−1.29

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; ^b $wR_2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 87.0434P]$, where $P = (F_o^2 + 2F_c^2)/3$.

[CeW₁₀O₃₆]}·6H₂O from an aqueous solution system. Compound **1** represents the first extended structure based on the [Ce(W₅O₁₈)₂]^{9−} polyoxoanion. This work demonstrates that many other interesting compounds with extended architectures can be obtained by using various POM clusters as building blocks. More work along this line is underway in our laboratory.

Experimental Section

Materials and methods

All chemicals purchased were of reagent grade and used without further purification. Na₄[W₁₀O₃₂] was prepared according to the literature method [24]. An FTIR spectrum was recorded in the range 400–4000 cm^{−1} on an Alpha Centaur FTIR spectrophotometer using a KBr pellet. Elemental analysis of N was performed on a Perkin-Elmer 2400 CHN elemental analyzer. Ce, W, Na, and Cl were determined by a Leaman inductively coupled plasma (ICP) spectrometer. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N₂ with a heating rate of 10 °C min^{−1}.

Synthesis

Freshly prepared Na₄[W₁₀O₃₂] (1.22 g, 0.5 mmol) was dissolved in 40 mL of an aqueous NaCl (0.117 g, 2.0 mmol)

Table 2. Selected bond lengths (Å) and bond angles (deg) for compound **1**^a.

W(1)–O(1)	1.734(13)	W(4)–O(11)	1.719(11)
W(1)–O(4)	1.753(19)	W(4)–O(12)	1.773(15)
W(1)–O(3)	1.920(9)	W(4)–O(10)	1.924(10)
W(1)–O(2)	2.035(16)	W(4)–O(13)	1.927(7)
W(1)–O(7)	2.3240(16)	W(4)–O(14)	2.029(14)
W(2)–O(5)	1.745(12)	W(4)–O(15)	2.3170(11)
W(2)–O(6)	1.771(18)	W(5)–O(16)	1.74(3)
W(2)–O(3)	1.942(9)	W(5)–O(14)	1.911(14)
W(2)–O(8)	2.009(15)	W(5)–O(15)	2.31(2)
W(2)–O(7)	2.3034(12)	W(5)–O(14) ^{#1}	1.911(14)
W(3)–O(9)	1.73(3)	Ce(1)–O(4)	2.481(19)
W(3)–O(8)	1.888(14)	Ce(1)–O(12)	2.496(13)
W(3)–O(2)	1.922(18)	Ce(1)–O(6)	2.504(16)
W(3)–O(7)	2.30(3)	O(20)–Na(2)	2.426(17)
O(1)–Na(1)	2.471(11)	O(21)–Na(2)	2.486(17)
O(17)–Na(1)	2.40(3)	O(22)–Na(2)	2.459(12)
O(23)–Na(1)	2.381(13)	O(21)–Na(3)	2.430(13)
O(24)–Na(1)	2.34(4)	O(25)–Na(3)	2.36(6)
O(18)–Na(2)	2.370(17)	Na(2)–Cl(1)	2.746(7)
O(19)–Na(2)	2.462(13)	Na(3)–Cl(1)	2.824(18)
O(1)–W(1)–O(2)	96.5(8)	O(16)–W(5)–O(14)	102.8(4)
O(3)–W(1)–O(2)	82.3(4)	O(16)–W(5)–O(15)	180
O(2)–W(1)–O(7)	74.4(9)	O(14)–W(5)–O(15)	77.2(4)
O(5)–W(2)–O(6)	102.9(7)	O(14)–W(5)–O(15)	77.2(4)
O(5)–W(2)–O(8)	96.5(7)	O(4)–Ce(1)–O(12)	76.9(4)
O(6)–W(2)–O(7)	85.8(8)	O(4)–Ce(1)–O(6)	73.4(3)
O(9)–W(3)–O(8)	102.8(4)	O(12)–Ce(1)–O(6)	142.3(3)
O(8)–W(3)–O(2)	87.16(15)	O(24)–Na(1)–O(23)	88.3(7)
O(8)–W(3)–O(7)	77.2(4)	O(24)–Na(1)–O(1)	97.1(7)
O(11)–W(4)–O(12)	103.4(6)	O(17)–Na(1)–O(1)	86.6(7)
O(12)–W(4)–O(10)	93.1(7)	O(18)–Na(2)–O(20)	85.8(6)
O(11)–W(4)–O(13)	103.1(5)	O(18)–Na(2)–O(22)	91.8(6)
O(25)–Na(3)–O(21)	91.9(5)	O(20)–Na(2)–O(19)	114.1(6)
O(21)–Na(3)–Cl(1)	88.1(5)	Na(2)–Cl(1)–Na(3)	84.2(3)

^a Symmetry transformations used to generate equivalent atoms: ^{#1} *x*, 1 − *y*, *z*.

solution with stirring. Then, a solution of Ce(NO₃)₃·6H₂O (0.217 g, 0.5 mmol) in distilled water (15 mL) was dropwise added. The pH value of the mixture was carefully adjusted to 4.8 using 1 M HCl. The final solution was heated to 80 °C for 1 h and then a solution of 4 M NH₄Cl (20 mL) was added to the reaction mixture at the same temperature. After being cooled to r. t., the final yellow suspension was filtered. The filtrate was kept for slow evaporation at r. t. The yellow columnar crystals of **1** were isolated after one week (yield 45 % based on W). Elemental analysis for H₇₀CeClN₃Na₇W₁₀O₆₇: calcd. Cl 1.05, N 1.25, Na 4.78, W 54.66, Ce 4.17; found Cl 1.29, N 1.42, Na 4.56, W 54.80, Ce 3.89.

X-Ray crystallography

A yellow single crystal with dimensions 0.31 × 0.26 × 0.23 mm³ was glued on a glass fiber. Data were collected on a Rigaku R-axis RAPID IP diffractometer at 293 K using graphite-monochromated MoK_α radiation (λ = 0.71073 Å)

and IP techniques in the range $3.21^\circ < \theta < 24.99^\circ$. An empirical absorption correction was applied. The structure was solved by Direct Methods and refined by full-matrix least-squares methods on F^2 using the SHELXS/L-97 crystallographic software package [25]. Anisotropic displacement parameters were used to refine all non-hydrogen atoms. The hydrogen atoms of NH_4^+ were located from difference Fourier maps and the other hydrogen atoms were included at idealized positions. Further details of the X-ray structural analysis are given in Table 1. Selected bond lengths and angles are listed in Table 2.

CSD 417858 contains the supplementary crystallographic data for this paper. This data may be obtained from

the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de).

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