

Crystal structures of the dinitrate-bis-(acetylenedicarboxylate) and acetylenedicarboxylate pseudorotaxane complexes of [24-pyrimidinium crown 6]

Christopher A. Waddling · Roger E. Cramer

Received: 5 April 2007 / Accepted: 16 June 2007 / Published online: 24 July 2007
© Springer Science+Business Media B.V. 2007

Abstract The reaction of [24-Pyrim C6][NO₃]₆ · 8H₂O with the monopotassium salt of acetylenedicarboxylic acid yielded single crystals of [24-Pyrim C6][C₄O₄]₂[NO₃]₂ · 7 H₂O, (**1**). The compound crystallized in the triclinic space group P $\bar{1}$, with $a = 9.731(8)$ Å, $b = 10.953(9)$ Å, $c = 14.270(14)$ Å, $\alpha = 108.06(7)^\circ$, $\beta = 94.86(7)^\circ$, $\gamma = 99.01(7)^\circ$, $Z = 1$, $R = 0.0737$, $R' = 0.1024$, and 3709 independent reflections. The reaction of [24-Pyrim C6]Cl₆ with the monopotassium salt of acetylenedicarboxylic acid gives single crystals of the inclusion complex {[24-Pyrim C6][C₄O₄]₂} · [C₄O₄]_{0.92} Cl_{0.17}[H₂C₄O₄]_{0.16} · 10H₂O, (**2**). The compound crystallizes in the triclinic space group P $\bar{1}$, with $a = 13.543(3)$ Å, $b = 14.354(8)$ Å, $c = 17.484(8)$ Å, $\alpha = 74.35(4)^\circ$, $\beta = 79.12(3)^\circ$, $\gamma = 69.77(3)^\circ$, $Z = 2$, $R = 0.0976$, $R' = 0.2662$, and 5655 independent reflections with. Strength of binding and size of the nitrate and chloride counter ions in the reacting species determines the mode of acetylenedicarboxylate binding to the cation upon crystallization.

Keywords Crystal structure · Pyrimidiniophane · Inclusion complex · Acetylenedicarboxylate

Introduction

The destruction of thiamin nitrate by sulfite ion, reported over seventy years ago [1], led Shimahara et al. to observe

that thiamin is degraded in refluxing methanol to give an oligomeric polypyrimidinium species [2]. The crystal structure of the resultant [24-Pyrim C6][NO₃]₆ indicates the presence of a hexapyrimidinium macrocycle surrounded by six equivalent nitrate ion positions [3], plus one minor nitrate ion position near the interior of the cavity. These positions were stabilized in part by electrostatic as well as hydrogen bonding interactions.

Although the diameter of the cavity of the [24-Pyrim C6]⁶⁺ cation, shown in Fig. 1, has been found to vary from 5.8 to 6.6 Å (as measured between opposite C(6)-H atoms) [3–5], the narrow cavity diameter allows only a few types of molecules or ions to be included at or about the central position. Complexes of this cation are often seen with the associated anion positioned either at the entrance to the cavity or associated with the outer portion of the cation, as in the [24-Pyrim C6][NO₃]₆ and [24-Pyrim C6][Pb(NO₃)₆][NO₃]₂ complexes [3, 5].

To form a stable inclusion complex of the [24-Pyrim C6]⁶⁺ cation, we have successfully utilized the air and water-stable acetylenedicarboxylate [6]. In this work, we present the crystal structures of two complexes of the [24-Pyrim C6]⁶⁺ cation with the acetylenedicarboxylate ion, one of which exhibits an external-only association complex (**1**), while the other is a pseudorotaxane (**2**). The nitrate counter-ion of the starting material used in the preparation of the external-only complex has been shown to bind strongly to the cation via multiple hydrogen-bond interactions [3], while the chloride counter-ion of the starting material used in the preparation of the pseudorotaxane complex is thought to interact weakly with the cation. In a basic competition between the anions in solution, the nitrate ion bars the acetylenedicarboxylate from forming an inclusion complex in (**1**), while the weakly bound chloride ion is easily displaced, leading to the pseudorotaxane (**2**).

C. A. Waddling (✉)
Department of Biochemistry, University of California,
San Francisco, 600 16th St., S126C, San Francisco,
CA 94158, USA
e-mail: waddling@msg.ucsf.edu

R. E. Cramer
Department of Chemistry, University of Hawaii,
2545 McCarthy Mall, Honolulu,
HI 96822, USA

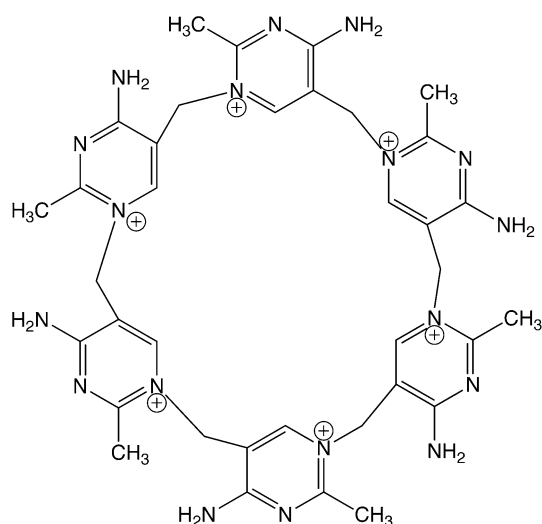


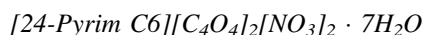
Fig. 1 Sketch of the [24-pyrimidinium crown 6]⁶⁺ cation

Experimental

Materials

[24-Pyrim C6][NO₃]₆ · 16H₂O was prepared as previously described [3]. Crude [24-Pyrim C6][Cl]₆ was prepared by ion exchange of [24-Pyrim C6][NO₃]₆ · 16H₂O with potassium chloride. Monopotassium acetylenedicarboxylic acid was used as purchased from Aldrich Chemical Co. All solvents were reagent grade, and were used without further purification. A Nicolet R3mv diffractometer was used to collect x-ray crystal data. A GE QE-300 FT spectrometer was used to obtain ¹H-NMR spectra in D₂O with sodium 3-(trimethylsilyl)-tetradeuteropropionate as reference.

Syntheses



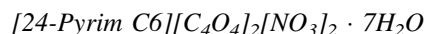
Crude [24-Pyrim C6][NO₃]₆ · 16H₂O [3] was placed in one end of a diffusion tube which was filled with deionized water. To the other end of the diffusion tube was added KHC₄O₄. After approximately three weeks, colorless, block-shaped crystals of the title compound were deposited near the [24-Pyrim C6][NO₃]₆ · 16H₂O end of the tube. The insoluble crystals were removed and determined to be [24-Pyrim C6][C₄O₄]₂[NO₃]₂ · 7H₂O, (**1**).



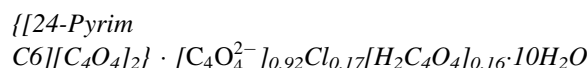
[24-Pyrim C6][Cl]₆ was placed in one end of a diffusion tube. To the other end was added KHC₄O₄. After approximately three weeks, colorless, parallelepiped-shaped

plates were deposited. The insoluble crystals were removed and found to be {[24-Pyrim C6][C₄O₄]₂} · [0.92Cl_{0.17}[H₂C₄O₄]_{0.16} · 10H₂O, (**2**), by x-ray diffraction.

X-Ray data collection and reduction

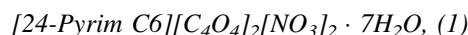


A crystal of (**1**) with dimensions of 0.36 × 0.42 × 0.45 mm was prepared as above and glued to a glass fiber, which was then fixed to the goniometer head. The unit cell was determined to be triclinic based on reflections with θ values between 7.5 and 15°. A total of 4020 reflections which fell into the $-10 < h < 10$, $-11 < k < 11$, and $0 < l < 15$ ranges were collected at room temperature, giving 3709 unique reflections with a merging *R* value of 7.34%. Three check reflections, which showed no decrease in intensity throughout data collection, were monitored after every 97th reflection. Table 1 lists a summary of crystal data and parameters.



A crystal of (**2**) with dimensions of 0.14 × 0.25 × 0.58 mm was prepared as above and glued to a glass fiber, which was then fixed to the goniometer head. The unit cell was determined to be triclinic based on reflections with θ values between 7.5 and 15°. A total of 6736 reflections which fell into the $0 < h < 13$, $-12 < k < 13$, and $-16 < l < 16$ ranges were collected at room temperature, giving 5655 unique reflections with a merging *R* value of 9.72%. Three check reflections, which showed no decrease in intensity throughout data collection, were monitored after every 97th reflection. Table 1 lists a summary of crystal data and parameters.

Structure solution and refinement



The structure of (**1**) was solved using the direct methods package of SHELX-86 [7] by increasing the minimum *E* value to 1.4. The solution with the best combined figure of merit showed all of the atoms of two and a half pyrimidinium units, one acetylenedicarboxylate ion, and one nitrate ion. These atoms were refined *via* least squares and a Fourier difference map was calculated, indicating the remainder of the third pyrimidinium ring and four water oxygen atoms. Hydrogen atoms were added in calculated positions and were allowed to ride on the atom to which they were attached. Hydrogen atoms on water oxygen

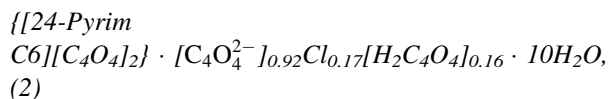
Table 1 Crystal data and structure refinement parameters^a

	[24-Pyrim C6] [C ₄ O ₄] ₂ [NO ₃] ₂ · 7H ₂ O ^b	{[24-Pyrim C6][C ₄ O ₄] ₂ } · [C ₄ O ₄] _{0.92} Cl _{0.17} [H ₂ C ₄ O ₄] _{0.16} · 10H ₂ O ^b
Empirical formula	C ₄₄ H ₆₁ N ₂₀ O ₂₁	C _{48.98} H _{68.75} C _{10.17} N ₁₈ O _{22.54}
Formula weight	1206.13	1276.54
Unit cell dimensions	a = 9.731(8) Å b = 10.953(9) Å c = 14.270(14) Å α = 108.060(10)° β = 94.86(7)° γ = 99.010(10)°	a = 13.543(3) Å b = 14.354(8) Å c = 17.484(8) Å α = 74.35(4)° β = 79.12(3)° γ = 69.770(10)°
Volume	1414(2) Å ³	3054(2) Å ³
Z	1	2
Density (calculated)	1.423 Mg/m ³	1.593 Mg/m ³
Absorption coefficient	0.115 mm ⁻¹	0.153 mm ⁻¹
F(000)	636	1552
Crystal size	0.36 × 0.42 × 0.45 mm	0.14 × 0.24 × 0.58 mm
θ range for data collection	1.99–22.55°	1.86–20.00°
Index ranges	–10 < h < 10, –11 < k < 11, 0 < l < 15	0 < h < 13, –12 < k < 13, –16 < l < 16
Reflections collected	4020	6736
Independent reflections	3709 (R _{int} = 0.0612)	5655 (R _{int} = 0.0723)
Data/restraints/parameters	3397/5/432	4342/276/850
Goodness-of-fit on F ²	0.959	0.912
Final R indices [I > 2σ(I)]	R1 = 0.0734, wR ² = 0.1914	R1 = 0.0972, wR ² = 0.2131
R indices (all data)	R1 = 0.1017, wR ² = 0.2077	R1 = 0.2666, wR ² = 0.2701
Largest diff. peak and hole	0.430 and –0.355 eÅ ⁻³	0.338 and –0.299 eÅ ⁻³

^a Temperature, 293(2) K; Wavelength, 0.71073 Å; Crystal system, Triclinic; Space group, P $\bar{1}$; Refinement method, Full-matrix least-squares on F²

^b Formula derived from refined structure

atoms O(1), O(2), and O(3) were then located and included in the atom list. The O(4) atom was split into two positions, O(4) and O(5). Because these atoms sat upon the inversion center and their combined occupancy was refining to slightly greater than the allowed 0.5, it was fixed to 0.50 using a group occupancy parameter. Anisotropic refinement of all non-hydrogen atoms except O(5) led to a final reduction of the *R* value to 7.34%. The asymmetric unit of (1), is shown in Fig. 2 [8].



The solution of this structure proceeded with great difficulty. To solve the structure, the direct methods package of SHELX-86 was employed [7]. The minimum *E* value was lowered from the default of 1.2 to 1.0. The number of phase relations was increased from 497 to 600, the number of solutions attempted was increased from 50 to 200, and the number of cycles of refinement on the initial solution

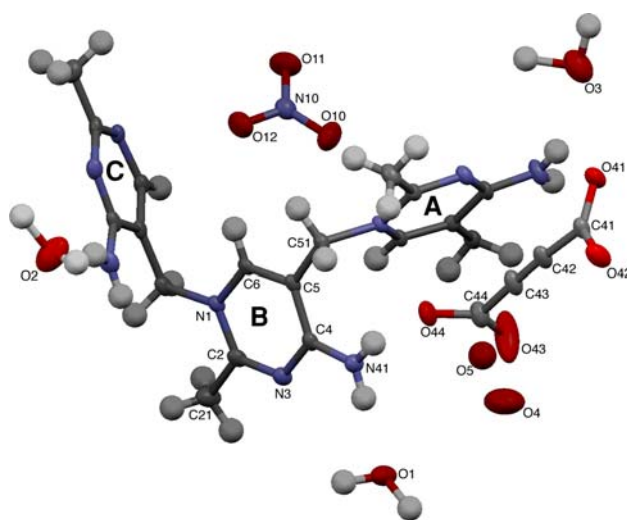
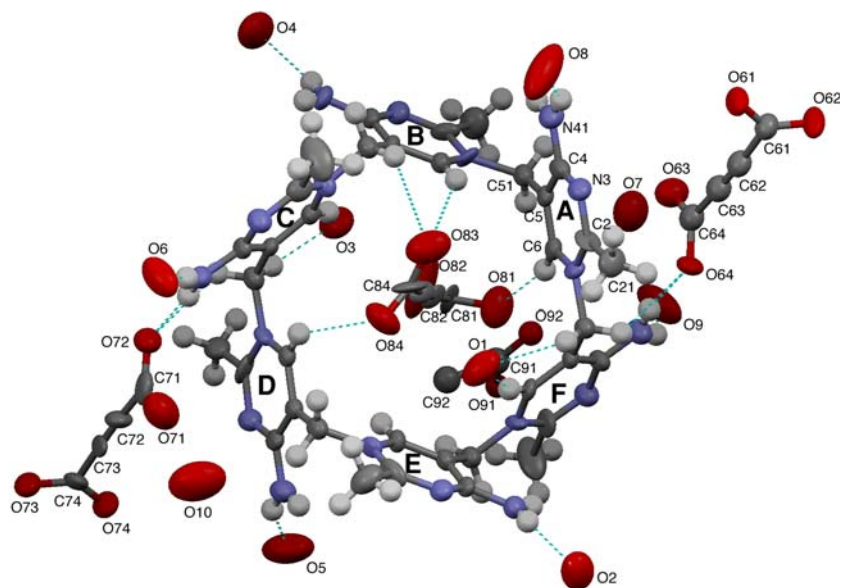


Fig. 2 Drawing of the asymmetric unit of (1) showing 50% probability thermal parameters (Figure generated with Mercury [8]). Minor water positions removed for clarity

was increased from 1 to 4 using FMAP 10. This gave a solution in which two pyrimidinium rings and their substituents were seen. Since the size of the unit cell required that an entire $[24\text{-Pyrim C6}]^{6+}$ cation be found, it was concluded that two of the six pyrimidinium groups was not enough to solve the structure by least squares. Thus, the eighteen atoms that were found were added to the instructions file and tangent expansion revealed one of the acetylenedicarboxylate anions and the remaining four pyrimidinium rings, completing the cation.

Generation of a Fourier difference map using SHELX-93 [9] revealed the few remaining pyrimidinium substituent atoms and a second acetylenedicarboxylate anion. A third anion, positioned at the center of the cation, was found after further refinement. Inclusion of the ten largest remaining peaks as water molecules lowered the *R*-value from 30 to 18%. There then appeared to be half of another acetylenedicarboxylate positioned on an inversion center between two cations. Inclusion of these atoms and refinement using a group occupancy parameter showed them to be an acetylenedicarboxylic acid, lowering *R* to 15.5%. The occupancies of the three anions and the acetylenedicarboxylic acid were allowed to refine. Nine fully occupied water oxygen atoms were located after subsequent iterations of least squares refinement. Three partially occupied water oxygen atoms were also located, one near the acetylenedicarboxylic acid position. A small amount of electron density located near the partially occupied dicarboxylic acid was included as a chloride ion, lowering *R* and the occupancy of the central acetylenedicarboxylate ion, to which the occupancy of the chloride ion was later tied using a SUMP instruction. This density was included as a chloride ion and not a water–oxygen atom so as to achieve charge balance in the complex.

Fig. 3 Drawing of the asymmetric unit of **(2)** showing 50% probability thermal parameters (Figure generated with Mercury [8]). Minor water positions removed for clarity



The addition of hydrogen atoms at calculated positions and their refinement using group thermal parameters, along with anisotropic refinement of all non-hydrogen atoms lead to a drop in *R* to 9.72%. The occupancies of the two outer acetylenedicarboxylate di-anions refined to just over 100%, and were thus fixed at full occupancy, giving a total charge of -4 for these anions. The dianion in the center of the cavity refined to 91.7(6)% (total charge $-1.83(2)$), the chloride ion to 17.4(11)% (total charge $-0.174(11)$), and the neutral, diprotonated acetylenedicarboxylic acid to 32.9(14)%. The $+6$ charge of the cation is thus balanced by the sum of the charges of the anions $[4 + 1.83(2) + 0.174(11) = 6.0(4)]$. It was necessary to fix the bond distances in the 32.9(14)% acetylenedicarboxylic acid using a DFIX instruction, as is often the case with partially occupied atoms. The ratio of data to parameters is low, making accurate anisotropic refinement difficult. Thus, it was necessary to restrain the thermal parameters of all similar atoms in the $[24\text{-Pyrim C6}]^{6+}$ cation using a SIMU instruction. It was also necessary to restrain the bond lengths and angles for the acetylenedicarboxylate anion using DFIX instructions for the same reason. The asymmetric unit of **(2)** is shown in Fig. 3.

Results

The structure of **(1)**

The asymmetric unit of **(1)** contains a fully occupied acetylenedicarboxylate ion, one fully occupied nitrate ion centered on a fully occupied nitrogen atom, but disordered over two orientations in a 93:7% ratio, and three fully and

one partially occupied water molecules, as shown in Fig. 2 [8]. $P\bar{1}$ symmetry operations generate a unit cell containing one [24-Pyrim C6]⁶⁺ cation, two fully occupied acetylenedicarboxylate ions, two fully occupied nitrate ions, and six fully occupied water sites, as shown in Fig. 4 [8].

Although the bond lengths and bond angles of the individual pyrimidinium groups of the cation in (1) are indistinguishable from those reported previously [3–5], there is an important structural difference in the ring. Measured with respect to the plane defined by the six C(6) atoms of the cation, the three unique pyrimidinium planes in (1) form angles of 70.4° (A), 67.5° (B), and 66.9° (C). By comparison, in the [24-Pyrim C6][NO₃]₆ · 16H₂O [3] and [24-Pyrim C6][M(NO₃)₆][NO₃]₂ (M = Pb or Ba, [5]) structures, the unique pyrimidinium plane forms an angle of 57.6° and 57.5°, respectively, with the C(6) plane. This increased dihedral angle has the effect of widening the diameter of the cavity (as measured between opposite C(6)–H atoms) from 5.86 Å in the previously reported structures to 6.59 Å in (1).

In the [24-Pyrim C6][NO₃]₆ · 16H₂O and [24-Pyrim C6][M(NO₃)₆][NO₃]₂ structures, two nitrate ions are associated 2.48 and 1.76 Å, respectively, above and below the center of the cation cavity [3, 5]. In the previously solved structures, the nitrate ions are coplanar with the cation, while in (1), the nitrate ions, located 1.79 Å from the centroid of the cation, are tipped 19.1° from the plane formed by the C(6) atoms of the cation. This tipped orientation brings O(11) closer to a symmetry equivalent O(2) water, making a strong O(2)–H···O(11) hydrogen bond of 1.95(5) Å and 160(8)°. In doing so, it moves the O(11) of the nitrate farther away from the C(6)A–H with which it associates, resulting in a C(6)A–H···O(11) distance of 2.71 Å. By comparison, the remaining two oxygen atoms of the nitrate ion associate more closely with the other two C(6)–H positions, with hydrogen bonding distances of 2.51 Å and 2.57 Å. Hydrogen-bond distances for (1) are listed in Table 2.

The dihedral angle between the two ends of the acetylenedicarboxylate ion in (1), at 89.0° is significantly greater than that previously reported [10–13]. Although buty-

nedioic acid dihydrate is reported to be planar, no crystal structure or spectroscopic evidence is presented to support this claim [10]. In the structure of the anhydrous buty-nedioic acid, the dihedral angle is reported to be 57.8°.

The structure of (2)

The asymmetric unit of the (2), shown in Fig. 3, consists of one complete [24-Pyrim C6]⁶⁺ cation, two fully occupied acetylenedicarboxylate anions, one 91.7(6)%-occupied acetylenedicarboxylate dianion, half of a 32.9(14)%-occupied neutral acetylenedicarboxylic acid, nine fully and three partially occupied water molecules, and a 17.4(11)% occupied chloride ion. Thus, the unit cell contains two [24-Pyrim C6]⁶⁺ cations, four fully occupied acetylenedicarboxylate anions, two 91.7(6)% occupied acetylenedicarboxylate anions at the center of the cation, one 32.9(1)%-occupied neutral acetylenedicarboxylic acid, eighteen fully and six partially occupied water molecules, and two 17.4(11)%-occupied chloride ions.

Dihedral angles of the six independent pyrimidinium groups (A–F) to the plane formed by the six C(6) atoms of the cation are: A—72.8°; B—64.7°; C—73.4°; D—66.2°; E—65.7°; F—66.3°. Rings B and E, positioned opposite one another, have the two shallowest planar dihedral angles. As a result, these two groups create the shortest cross-cation C(6)–H···H–C(6) distance in (2) of 6.64 Å.

The included dicarboxylate forms a pseudorotaxane complex with the cation, asymmetrically associating with the host. Inclusion is stabilized by C(6)–H···O hydrogen bonds to three of the four dicarboxylate oxygen atoms, with C(6)–H···O distances ranging from 2.33 to 2.52 Å. Hydrogen-bond distances for (2) are listed in Table 3.

The dihedral angles of the four acetylenic moieties, represented as three dicarboxylate ions and one dicarboxylic acid, are significantly different from one another, as shown in Table 4. The anions are similar to that seen in the previous structure, with dihedral angles ranging from 72.9° for the included anion to 82.4° for one of the exterior anions. The partially occupied dicarboxylic acid, unlike the anhydrous acid reported [10], is planar, as is a necessary

Fig. 4 Stereo drawing of (1) showing 50% probability thermal parameters (Figure generated with Mercury [8]). Minor water positions removed for clarity

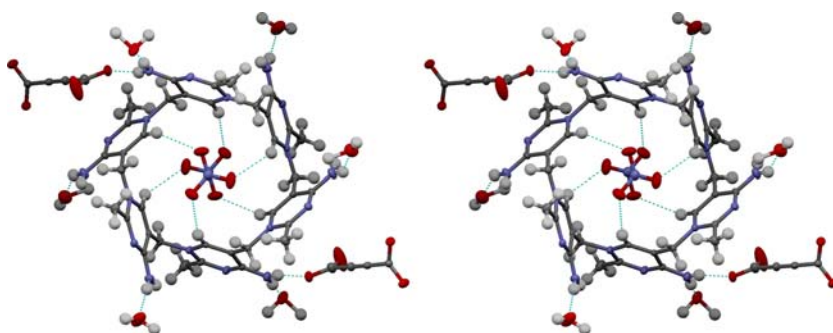


Table 2 Hydrogen bonding distances [Å] and angles [°] in **(1)**

D–H...A	D–H	H...A	D...A	D–H...A
N41A–H41A...O3	0.86	2.16	2.916 (7)	147
N41A–H41B...O41 ^b	0.86	2.07	2.904 (6)	165
N41B–H41C...O1	0.86	1.98	2.834 (5)	172
N41B–H41D...O44	0.86	2.00	2.843 (5)	166
N41C–H41E...O2	0.86	2.02	2.873 (6)	169
N41C–H41F...O42 ^a	0.86	1.95	2.797 (6)	166
O2–H2A...O11 ^c	0.96 (4)	1.95 (5)	2.871 (7)	160 (8)
O2–H2A...O11A ^c	0.96 (4)	1.78 (8)	2.68 (5)	154 (9)
O2–H2A...O12 ^c	0.96 (4)	2.70 (6)	3.553 (8)	148 (7)
O2–H2B...O3 ^d	0.85 (4)	2.12 (6)	2.925 (8)	158 (9)
O3–H3A...O1 ^e	1.03 (4)	2.52 (9)	2.902 (7)	101 (6)
O3–H3A...O2 ^f	1.03 (4)	2.77 (9)	2.925 (8)	88 (5)
O3–H3B...O4 ^e	0.93 (4)	2.18 (9)	2.774 (19)	121 (7)
O3–H3B...O5 ^e	0.93 (4)	1.75 (8)	2.55 (4)	142 (8)
O3–H3B...O43 ^b	0.93 (4)	2.18 (6)	2.869 (8)	130 (7)
C6A–H6A...O11 ^g	0.93	2.71	3.544 (6)	149
C6B–H6B...O12	0.93	2.51	3.379 (7)	156
C6C–H6C...O10 ^g	0.93	2.57	3.322 (8)	138

Symmetry codes: ^a–x, –y+2, –z; ^b–x–1, –y + 1, –z; ^c–x, –y + 3, –z + 1; ^dx + 1, y + 1, z; ^ex–1, y, z; ^fx–1, y–1, z; ^g–x, –y + 2, –z + 1

condition due to its position on the crystallographic center of inversion. This is more akin to the dihydrate of the dicarboxylic acid, which is also reported to be planar [10].

Discussion

Inclusion vs. Addition

The differences in binding modes of the dicarboxylate ions in the two structures may be explained by observations made during crystallization trials of the pure hexanitrate and hexahalide salts of the [24-Pyrim C6]⁶⁺ cation. In attempts to crystallize salts of the [24-Pyrim C6]⁶⁺ cation, it has been found that both the hexanitrate and the hexaiodide crystallize easily from an aqueous solution. Conversely, the bromide and chloride salts do not form well-defined crystals, instead precipitating from solution as amorphous solids. All attempts at crystallization using a variety of methods and solvents have failed. We hypothesize that the smaller halides may be too small to form enough close contacts with the cation to crystallize. Conversely, the larger iodide [14] and nitrate ions have more steric contact with the cation, and as a result are stabilized through hydrogen bonding and easily crystallized.

The crystal structures of the [24-Pyrim C6][NO₃]₆ · 16 H₂O [3], [24-Pyrim C6][Pb(NO₃)₆][NO₃]₂ [5], and [24-Pyrim C6][I]₆ · 8H₂O species [14] reveal that anions are positioned at either side of the opening leading to the center of the cation. In the case of the hexanitrate salt, each position is 18.0(9) % occupied [3], while in the [24-Pyrim

C6][Pb(NO₃)₆][NO₃]₂ structure, this position is 83(2)% occupied [5].

While the hexanitrate species shows only minor association between the interior of the cation and anion [3], in the [24-Pyrim C6][Pb(NO₃)₆][NO₃]₂ structure, the nitrate ions are tightly bound to the interior of the cation, forming very strong hydrogen bonds with the C(6)–H atoms. Similarly, in **(1)**, the three major nitrate oxygen positions form C–H...O hydrogen bonds with H...O bond lengths of 2.51, 2.57, and 2.72 Å and bond angles from 138 to 155°, with the nitrate ions positioned closer to the centroid of the cation than in the hexanitrate species. This preference for nitrate ions over the dicarboxylate results in the addition complex seen in **(1)**.

Conversely, the inclusion complex **(2)** that results from the reaction of the hexachloride species with the acetylenedicarboxylate indicates that the center of the cation must exhibit a lower affinity for a chloride ion, thus preferentially encavitating the dicarboxylate ion instead.

Pseudorotaxane acetylenedicarboxylate ion stabilization

The partially occupied acetylenedicarboxylic acid situated on an inversion center and between adjacent cations in **(2)** strongly hydrogen bonds to the pseudorotaxane acetylenedicarboxylate anion, with a short O...O distance of 2.50 Å. Hydrogen bonding between the included anion and the [24-Pyrim C6]⁶⁺ cation itself also helps to stabilize the structure of the included species. One strong and two weak hydrogen bonds are formed between the aromatic C(6)–H

Table 3 Hydrogen bonding distances [Å] and angles [°] in (2)

D–H...A	D–H	H...A	D...A	D–H...A
N41A–H41A...O74 ^a	0.86	2.09	2.927 (14)	164
N41A–H41B...O8	0.86	2.14	2.917 (14)	149
N41B–H41D...O62 ^b	0.86	1.99	2.817 (13)	161
N41B–H41C...O4	0.86	2.12	2.867 (13)	145
N41C–H41F...O72	0.86	1.96	2.808 (13)	167
N41C–H41E...O6	0.86	1.99	2.851 (14)	175
N41D–H41G...O5	0.86	2.15	2.918 (15)	149
N41D–H41H...O61 ^c	0.86	2.14	2.966 (14)	161
N41E–H41I...O2	0.86	2.15	2.955 (13)	157
N41E–H41J...O73 ^d	0.86	1.93	2.759 (13)	162
N41F–H41K...O9	0.86	2.38	3.119 (18)	144
N41F–H41K...O11	0.86	2.20	3.03 (4)	162
N41F–H41L...O64	0.86	2.04	2.877 (12)	165
C6A–H6A...O81	0.93	2.33	3.217 (16)	161
C6B–H6B...O83	0.93	2.52	3.243 (17)	135
C6C–H6C...O3	0.93	2.52	3.383 (15)	154
C6D–H6D...O84	0.93	2.47	3.187 (16)	134
C6E–H6E...O12	0.93	2.47	3.34 (3)	156
C6F–H6F...O1	0.93	2.34	3.234 (14)	161
C21D–H21L...O72	0.96	2.72	3.353 (15)	124
C21D–H21J...O9 ^e	0.96	2.63	3.529 (16)	156
C21E–H21N...O1 ^f	0.96	2.46	3.306 (16)	147
C21F–H21R...O73 ^d	0.96	2.60	3.267 (17)	127
C51B–H51D...O83	0.97	2.54	3.161 (16)	122
C51B–H51C...O62 ^b	0.97	2.44	3.116 (15)	126
C51C–H51E...O72	0.97	2.69	3.290 (15)	120
C51C–H51F...O3	0.97	2.47	3.404 (15)	162
C51E–H51I...O12	0.97	2.55	3.47 (3)	158
C51E–H51J...O73 ^d	0.97	2.60	3.222 (15)	122
C51F–H51L...O1	0.97	2.53	3.403 (15)	150
C51F–H51K...O64	0.97	2.65	3.247 (14)	120

Symmetry codes: ^a $x-1, y+1, z$;
^b $x, y-1, z$; ^c $x+1, y-1, z$; ^d $x,$
 $y+1, z$; ^e $-x+2, -y+2, -$
 $z+1$; ^f $-x+2, -y+2, -z+2$

Table 4 Dihedral angles between carboxylate end groups in butyrenedioic acid derivatives, (1), and (2)

Compound	Dihedral Angle [°]
HOCCCCOOH · 2H ₂ O ^{11–13}	0
HOCCCCOOH ^{11–13}	57.8
KOCCCCOOH ^{1°}	66.5
(1)	89.0
(2)	73.5 (pseudorotaxane)
	77.3 (external)
	82.4 (external)
	0 (dicarboxylic-acid)

of the cation and the oxygen atoms of the carboxylate end groups on the included anion, as indicated by the C(6)–H...O distances listed in Table 3. C–H...O hydrogen bonding has long been shown to be one of the driving

forces behind pseudorotaxane stabilization [15]. In (2), these C–H...O interactions to the included anion range from 2.33 to 2.52 Å, with bond angles of 134 to 161°. The anion is tipped 16.8° away from the axis which runs perpendicular to the six C(6) atoms of the cation and toward the strongest of the three interactions C(6)–H...O interactions.

Conclusions

It is apparent from this work that it is possible to prepare a pseudorotaxane complex of the [24-Pyrim C6]⁶⁺ cation. The formation of these complexes is driven by the affinity of the cation for the included species over that of the halide originally associated with the cation. The hexachloride starting material gives inclusion complexes in which 91.7(6)% of the cavities are occupied in the crystal struc-

ture by the acetylenedicarboxylate ion. Conversely, the nitrate ions have more affinity for the center of the cation than the linear dicarboxylate ion, preventing inclusion complex formation with the hexanitrate as the starting material. Hydrogen bonding between the aromatic hydrogen atoms of the cation and the carboxylate groups on the anion results in a high degree of stabilization in the inclusion complex.

The crystals used in this study, while adequate, did not diffract optimally under the room temperature data collection conditions, leading to high values of R_{int} for both datasets. The preparation of higher quality crystals coupled with cryogenic data collection will allow us to more accurately determine the structure of these complexes.

Future studies on the [24-Pyrim C6]⁶⁺ cation will focus on the route to inclusion complex formation. Preliminary results indicate that it may occur through opening of the [24-Pyrim C6]⁶⁺ ring, followed by association of the included species, and then closure of the cation around the guest molecule. These studies are proceeding with alkyne- α,ω -diols as the guest molecule.

Further stabilization of the anion within the cavity may be accomplished through termination of the carboxylate end groups by transition metal centers. Iron(II), cobalt(II), nickel(II), copper(I), and zinc(II) have been shown to form complexes with the acetylenedicarboxylic acid from aqueous solutions [6]. These complexes are thought to be polymeric with what appears to be repeating chains of the metal and the acetylenedicarboxylate ion. Reaction of these species in solution with the [24-Pyrim C6]⁶⁺ cation prior to their precipitation may lead to the desired complex. Work in this direction are currently underway in our laboratory.

References

- Williams, R.R.: Structure of vitamin B. *J. Am. Chem. Soc.* **57**, 229–230 (1935).

- Shimahara, N., Aaskawa, H., Kawamatsu, Y., Hirono, H.: Decomposition of thiamine in alcohol solution. II. *Chem. Pharm. Bull.* **22**(9), 2086–2090 (1974).
- Cramer, R.E., Waddling, C.A., Fujimoto, C.H., Smith, D.W., Kim, K.E.: Crystal structures of the nitrate salt of 24-Pyrimidinium crown 6 and its degradation product in Water–Methanol mixtures. *J. Chem. Soc., Dalton Trans.* 1675–1683 (1997).
- Cramer, R.E., Carrie, M.J.: Structure of (24-pyrimidinium crown-6)[(DMSO)HgI₃][HgI₄][Hg₂I₇] · 11DMSO · 2H₂O. *Inorg. Chem.* **29**, 3902–3904 (1990).
- Cramer, R.E., Mitchell, K.A., Hirazumi, A.Y., Smith, S.L.: Crystal structures of [Pb(NO₃)₆]⁴⁻ and [Ba(NO₃)₆]⁴⁻ salts of 24-pyrimidinium crown 6 {5,12,19,26,33,40-hexaamino-3,10,17,24,31,38-hexamethyl [1.6](1,5)pyrimidinophane}. *J. Chem. Soc., Dalton Trans.* 563–569 (1994).
- Allan, J.R., Beaumont, P.C., MacIndoe, L., Milburn, G.H.W., Werninck, A.: Thermal studies on acetylenedicarboxylic acid compounds of iron(II), cobalt(II), nickel(II), copper(II) and zinc(II). *Thermochimica Acta* **117**, 51–58 (1987).
- Sheldrick, G.M.: Phase annealing in SHELX-90: direct methods for larger structures. *Acta Crystallogr. A* **46**, 467–473 (1990).
- Macrae, C.F., Edgington, P.R., McCabe, P., Pidcock, E., Shields, G.P., Taylor, R., Towler, M., van de Streek, J.: Mercury: visualization, analysis of crystal structures. *J. Appl. Cryst.* **39**(3), 453–457 (2006).
- Sheldrick, G.M.: SHELXL 93. University of Göttingen (1993).
- Benghiat, V., Leiserowitz, L., Schmidt, G.M.J.: Molecular packing modes. VII. Crystal and molecular structures of anhydrous acetylenedicarboxylic acid. *J. Chem. Soc., Perkin Trans.* **2**(12), 1769–1772 (1972).
- Dubler, E., Linowsky, L.: Proof of the existence of a linear, centrosymmetric polyiodide ion I₇⁴⁻. Crystal structure of tetraamine copper(II) tetraiodide. *Helv. Chim. Acta* **58**(8), 2604–2609 (1975).
- Hon, P.K., Mak, T.C.W., Trotter, J.: Synthesis and structure of 1-methyl-1,3,5,7-tetraazaadamantan-1-ium octaiodide, [(CH₂)₆N₄CH₃]₂I₈. A new outstretched Z configuration for the polyiodide ion I₈²⁻. *Inorg. Chem.* **18**(10), 2916–2918 (1979).
- Rabenau, A., Shultz, H., Stoeger, W.: A polyiodide with regular I₄²⁻ chains: thallium lead iodide (Tl₆PbI₁₀). *Naturwissenschaften*, **63**(5), 245 (1976).
- Waddling, C.A.: Ph.D. Thesis, University of Hawaii (1998).
- Asakawa, M., Ashton, P.R., Brown, G.R., Hayes, W., Menzer, S., Stoddart, J.F., White, A.J.P., Williams, D.J.: Hydrogen-bonded pseudopolyrotaxanes. *Adv. Mater.* **8**(1), 37–41 (1996).