

removed, we expect this complex to be paramagnetic with a value close to the spin-only value of 3.87 Bohr magnetons.

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Structure of Tetrasodium 1,4,5,8-Naphthalenetetracarboxylate Octahydrate

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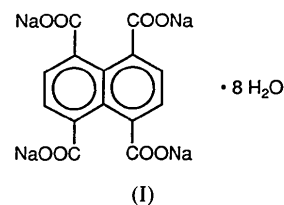
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Abstract. $\text{Na}_4[\text{C}_{14}\text{H}_4\text{O}_8]\cdot 8\text{H}_2\text{O}$, $M_r = 536.3$, monoclinic, $P2_1/n$, $a = 6.142$ (1), $b = 8.144$ (3), $c = 20.527$ (4) Å, $\beta = 93.97$ (1)°, $V = 1024.4$ (5) Å³, $Z = 2$, $D_x = 1.74$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 2.14$ cm⁻¹, $F(000) = 552$, $T = 295$ K, $R = 0.039$ for 1769 unique reflections having $I > \sigma_f$. In this structure, the title compound has an inversion center at the midpoint of the central naphthalene ring bond. The average C—C bond length in the naphthalene core is 1.41 (3) Å; the average interior angle is 119.9 (1.0)°. The exterior angle at the central naphthalene carbon is 122.7 (3)°, significantly smaller than in 1,8-substituted naphthalenes. The two inequivalent carboxyl groups adopt a non-planar arrangement with respect to the naphthalene core, making an average dihedral angle of 53.8 (1)° with it. The two inequivalent sodium ions have quite different environments. Na(1) is coordinated by six O atoms in a highly distorted octahedral arrangement with an average Na—O distance of 2.44 (10) Å. Na(2) is coordinated by five O atoms in a highly distorted trigonal bipyramidal arrangement with an average Na—O distance of 2.36 (3) Å. Each of the eight inequivalent water H atoms is involved in a single hydrogen bond. The average H...O (acceptor) distance is 2.00 (5) Å, the average O...O (acceptor) distance is 2.85 (5) Å and the average O—H...O (acceptor) angle is 165 (8)° for these hydrogen bonds. The average equivalent isotropic displacement parameter for the C and O atoms in the present

structure is less than half the corresponding value for typical organic structures.

Introduction. As part of a series of investigations of hydrogen bonding in organic solids, investigation of the structure of 1,4,5,8-naphthalenetetracarboxylic acid became of interest. We report here an investigation of crystalline tetrasodium 1,4,5,8-naphthalenetetracarboxylate octahydrate (I) whose structure has not previously been described.



Experimental. 1,4,5,8-Naphthalenetetracarboxylic acid obtained from Aldrich Chemical Company was suspended in water and reacted with excess analytical reagent grade NaOH to prepare an aqueous solution of tetrasodium 1,4,5,8-naphthalenetetracarboxylate. The solution was then purified by mixing it with Norit-A decolorizing carbon followed by filtration. The sodium salt thus purified was twice recrystallized from water by slow evaporation at room temperature to provide the experimental sample, a clear rectangular prism with approximate principal dimensions 0.23 × 0.23 × 0.38 mm. This was mounted on a glass rod with epoxy cement and coated with

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Apiezon L grease; data were collected at room temperature with a Rigaku AFC5S diffractometer utilizing monochromated Mo $K\alpha$ radiation.

The crystal system was found to be monoclinic. Unit-cell parameters were obtained from a symmetry-restricted least-squares fit of the setting angles for 25 centered reflections with $29 < 2\theta < 30^\circ$. Intensity data were measured for 2737 reflections (exclusive of standards) with $+h$, $+k$, $\pm l$ indices ($h_{\max} = 7$, $k_{\max} = 10$, $l = -26$ to 26) and 2θ values in the range $4 < 2\theta < 55^\circ$. The ω -scan technique was employed with scan widths $(1.20 + 0.35\tan\theta)^\circ$ in ω , and a background/scan time-ratio of 0.5. A variance was assigned to each reflection by means of the formula $\sigma_I^2 = \sigma_{cs}^2(I) + (0.03I)^2$ where σ_{cs} is based on counting statistics and I is the integrated intensity. Six standard reflections (10 $\bar{3}$, 121, 017, 15 $\bar{7}$, 415, 2,3,10) were measured after every 150 reflections; over the course of the intensity data collection they showed, on average, a relative intensity decay of 11.1%. A linear correction was applied to account for this decay. The data were corrected for Lorentz and polarization effects. A ψ -scan absorption correction was applied based on ψ -scan data obtained near the end of data collection; the range of transmission factors was 0.951–1.000, with an average value of 0.971. Averaging equivalent reflections then gave 2511 independent reflections with $R_{\text{int}} = 0.024$.

Among primitive monoclinic space groups, the observed systematic absences ($h0l$, $h + l = \text{odd}$; $0k0$, $k = \text{odd}$) uniquely determine the space group as $P2_1/n$. The direct methods program *SHELXS86* (Sheldrick, 1985) was used to generate an E map from which the initial positions of the inequivalent C and O atoms of the 1,4,5,8-naphthalenetetracarboxylate portion of the structure were assigned. Fourier difference methods were used to locate the positions of the two inequivalent Na atoms, the four inequivalent O atoms of the water molecules and the H-atom positions. Since the tetrasodium 1,4,5,8-naphthalenetetracarboxylate octahydrate unit contains a center of inversion at the midpoint of the C(5)—C(5') bond, the atomic positions listed above represent the asymmetric unit. Full-matrix least-squares refinement was performed (*TEXSAN*; Molecular Structure Corporation, 1989) to minimize the function $\sum \sigma_F^{-2} (|F_o| - |F_c|)^2$ in which $\sigma_F = \sigma_I/2FLp$. Neutral-atom scattering factors and anomalous-dispersion factors were taken from Cromer & Waber (1974) for C, O and Na; the scattering factor for hydrogen was taken from Stewart, Davidson & Simpson (1965).

The results of the final refinement cycle were: 1769 observations having $I > \sigma_I$, 194 variables; $R = 0.039$; $wR = 0.042$; $w = \sigma_F^{-2}$; $S = 1.38$; $(\Delta/\sigma)_{\max} < 0.01$. Max. and min. peaks on the final electron density difference map had values $+0.33$ and $-0.31 \text{ e } \text{\AA}^{-3}$

respectively. The max. peak was located at (0.78, -0.13 , -0.09), approximately halfway between C(1) and C(4); the min. peak was located at (0.30, 0.38, 0.20), 0.4 Å from Na(1). [For the final refinement cycle for 1654 independent observations having $I > 3\sigma_I$: $R = 0.036$, $wR = 0.041$; $S = 1.38$; $(\Delta/\sigma)_{\max} < 0.01$. Similarly, for the final refinement cycle for $I > 0$: $R = 0.053$; $wR = 0.044$; $S = 1.31$; $(\Delta/\sigma)_{\max} < 0.01$. These latter results are for comparison purposes only.]

Final atomic coordinates, equivalent isotropic and isotropic displacement parameters and their uncertainties are given in Table 1.* The hydrocarbon portion of the molecule is shown in Fig. 1 with selected interatomic distances specified in one asymmetric unit and angles in the other. Table 2 lists selected distances and angles in the coordination polyhedra of the two inequivalent sodium ions together with distances and angles for the four inequivalent water molecules.

Discussion. Bond lengths and angles for the 1,4,5,8-naphthalenetetracarboxylate anion are shown in Fig. 1. To date, neither the structure of the tetracarboxylic acid nor the structure of any other naphthalate anion has been determined. However, the structure of 1,8-naphthalenedicarboxylic acid (Fitzgerald, Gallucci & Gerkin, 1991) provides a basis for some interesting comparisons to the naphthalenetetracarboxylate anion.

The average C—C bond length for the naphthalene core of the anion is 1.41 (3) Å; the average interior angle is 119.9 (1.0)°. The values for 1,8-naphthalenedicarboxylic acid are similar at 1.40 (3) Å and 119.9 (1.8)° respectively. With an inversion center at the midpoint of the C(5)—C(5') bond, the pattern of bond lengths and angles in the naphthalene core of the anion is not exactly the same as the pattern in 1,8-naphthalenedicarboxylic acid, which has pseudo C_2 symmetry. In general, though, the bonds (present numbering) C(4)—C(5), C(5)—C(6) and C(5)—C(5') are the longest while bonds C(3)—C(4) and C(6)—C(7) are the shortest for both molecules. The exterior angles at C(4) and C(6) deviate from 120° in such a way as to cause the carboxyl groups to splay apart from each other in a manner similar to that observed in 1,8-naphthalenedicarboxylic acid and other naphthalenes substituted at the 1 and 8 positions (Akopyan, Kitaigorodskii & Struchkov, 1965; Einspahr, Robert, Marsh & Roberts, 1973; Fitzgerald, Gallucci & Gerkin, 1991).

* Lists of structure factors, anisotropic displacement parameters and tables of least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54278 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and equivalent isotropic and isotropic displacement parameters (\AA^2) for tetrasodium 1,4,5,8-naphthalenetetracarboxylate octahydrate.

E.s.d.'s are given within parentheses.

$$B_{eq} = (8\pi^2/3) \sum_i U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	B_{eq}/B
Na(1)	0.3366 (1)	-0.3998 (1)	-0.19002 (4)	1.87 (4)
Na(2)	-0.1750 (2)	0.2590 (1)	-0.16344 (5)	2.09 (4)
O(1)	-0.3323 (2)	-0.2846 (2)	-0.14613 (7)	1.55 (6)
O(2)	-0.3052 (2)	-0.0127 (2)	-0.16021 (7)	1.67 (6)
O(3)	0.1496 (3)	-0.1581 (2)	-0.15966 (7)	1.60 (6)
O(4)	0.1415 (2)	0.1049 (2)	-0.19144 (7)	1.52 (6)
O(5)	-0.0381 (3)	-0.4996 (2)	-0.21052 (8)	1.86 (7)
O(6)	0.4745 (3)	-0.6673 (2)	-0.20488 (8)	1.85 (7)
O(7)	-0.2089 (3)	0.4255 (3)	-0.0719 (1)	2.85 (9)
O(8)	0.2158 (3)	-0.4172 (3)	-0.06848 (9)	2.67 (8)
C(1)	-0.2812 (3)	-0.1418 (3)	-0.1271 (1)	1.15 (8)
C(2)	0.1402 (3)	-0.0062 (3)	-0.1485 (1)	1.17 (8)
C(3)	-0.3264 (4)	-0.1901 (3)	-0.0113 (1)	1.51 (8)
C(4)	-0.1987 (3)	-0.1208 (2)	-0.0561 (1)	1.11 (7)
C(5)	-0.0166 (3)	-0.0192 (2)	-0.0343 (1)	1.01 (7)
C(6)	0.1334 (3)	0.0467 (2)	-0.0780 (1)	1.14 (8)
C(7)	0.2939 (4)	0.1540 (3)	-0.0554 (1)	1.59 (8)
H(1)	-0.441 (4)	-0.255 (3)	-0.027 (1)	1.6 (5)*
H(2)	0.397 (4)	0.198 (3)	-0.085 (1)	2.3 (6)*
H(3)	-0.132 (5)	-0.419 (4)	-0.197 (1)	3.3 (7)*
H(4)	-0.076 (4)	-0.508 (3)	-0.248 (1)	2.6 (6)*
H(5)	0.445 (6)	-0.665 (4)	-0.249 (2)	5.3 (9)*
H(6)	0.376 (5)	-0.737 (4)	-0.196 (2)	4.4 (8)*
H(7)	-0.271 (5)	0.515 (4)	-0.084 (1)	3.6 (7)*
H(8)	-0.238 (6)	0.416 (5)	-0.031 (2)	6.8 (10)*
H(9)	0.176 (6)	-0.322 (4)	-0.085 (2)	5.2 (10)*
H(10)	0.097 (6)	-0.483 (4)	-0.072 (2)	4.8 (9)*

* Refined isotropically.

However, 1,8-naphthalenedicarboxylic acid and the other 1,8-substituted naphthalenes have values greater than 125° for the C(4)—C(5)—C(6) angle while the corresponding value for the 1,4,5,8-naphthalenetetracarboxylate anion is $122.7(3)^\circ$. The smaller angle at C(5) and C(5') is apparently a result of interactions on both sides of the naphthalene ring that limit the degree of distortion the molecule can readily undergo to accommodate the neighboring substituents. As a result, the C(4)⋯C(6) separation and the C(1)⋯C(2) separation for the tetracarboxylate anion are smaller than the same separations in the diacid: $2.521(3) \text{ \AA}$ for C(4)⋯C(6) in the tetracarboxylate anion vs $2.556(5) \text{ \AA}$ for the diacid; $2.875(3) \text{ \AA}$ for C(1)⋯C(2) in the tetracarboxylate anion vs $2.989(5) \text{ \AA}$ for the diacid.

The ten C atoms comprising the naphthalene core of the tetracarboxylate anion have an average deviation of 0.028 \AA from the best least-squares plane describing the naphthalene core. The corresponding value for 1,8-naphthalenedicarboxylic acid is 0.055 \AA . The two inequivalent carboxyl C atoms C(1) and C(2) deviate by -0.334 and $+0.281 \text{ \AA}$, respectively, from the least-squares plane of the naphthalene core. The planes of the two inequivalent carboxyl groups C(1), O(1), O(2) and C(2), O(3), O(4) make dihedral angles $52.5(1)$ and $55.1(1)^\circ$, respectively, with the best plane of the naphthalene core. These values are to be compared with $42.0(2)$

Table 2. Bond lengths (\AA) and angles ($^\circ$) for sodium coordination polyhedra and water molecules in the title compound

E.s.d.'s are given within parentheses.

Coordination polyhedron I			
Na(1)—O(1 ^{iv})	2.361 (2)	Na(1)—O(5)	2.450 (2)
Na(1)—O(3)	2.384 (2)	Na(1)—O(6)	2.365 (2)
Na(1)—O(4 ⁱⁱⁱ)	2.447 (2)	Na(1)—O(8)	2.656 (2)
Mean Na(1)—O	2.444 (101)		
Coordination polyhedron II			
Na(2)—O(2)	2.355 (2)	Na(2)—O(6')	2.338 (2)
Na(2)—O(4)	2.417 (2)	Na(2)—O(7)	2.339 (2)
Na(2)—O(5 ⁱⁱ)	2.371 (2)		
Mean Na(2)—O	2.364 (29)		
Water molecules			
O(5)—H(3)	0.93 (3)	O(7)—H(7)	0.86 (3)
O(5)—H(4)	0.78 (3)	O(7)—H(8)	0.87 (4)
O(6)—H(5)	0.92 (4)	O(8)—H(9)	0.88 (4)
O(6)—H(6)	0.86 (3)	O(8)—H(10)	0.91 (4)
Mean O—H	0.88 (4)		
Symmetry code: (i) $-x, -y, -z$; (ii) $1+x, y, z$; (iii) $\frac{1}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}-z$; (iv) $x, 1+y, z$; (v) $-1+x, 1+y, z$.			

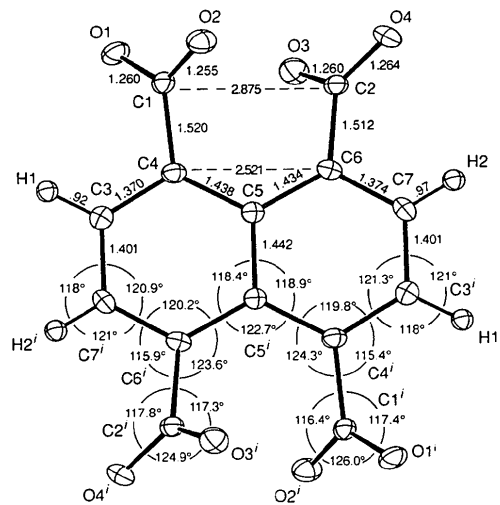


Fig. 1. An ORTEP (Johnson, 1976) view of the 1,4,5,8-naphthalenetetracarboxylate anion, with our numbering scheme. Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. An inversion center lies at the midpoint of the C(5)—C(5') bond. Bond lengths (\AA) and angles ($^\circ$) are shown. The e.s.d.'s for bond lengths and angles involving C and O are 0.003 \AA and 0.3° , respectively; for bond lengths and angles involving H, 0.03 \AA and 2° .

and $43.2(2)^\circ$ for the corresponding angles of the two inequivalent carboxyl groups in 1,8-naphthalenedicarboxylic acid. The carboxyl group planes form a $27.5(4)^\circ$ dihedral angle with each other because of the splaying apart described above; in 1,8-naphthalenedicarboxylic acid the corresponding value is $32.4(6)^\circ$. Fig. 2 shows the orientations the two inequivalent carboxyl groups adopt with respect to the naphthalene core.

Fig. 2 also depicts the coordination around the two inequivalent sodium ions and is a view of the title compound in the plane of the naphthalene core along the C(5)—C(5') bond. Table 2 lists selected distances and angles for atoms involved in coordination of the inequivalent Na atoms. Na(1) is coordinated by six O atoms in a distorted octahedron: three of the O atoms are carboxylate O atoms from three different naphthalenetetracarboxylate anions and the remainder are water O atoms. The average Na(1)—O distance is $2.44(10)$ Å with Na(1)—O(8) being noticeably larger than the other five Na—O distances. Na(2) is coordinated by five O atoms in a distorted trigonal bipyramid: two of the O atoms are carboxylate O atoms, both from the same naphthalenetetracarboxylate anion, and the remaining three O atoms are water O atoms. The average Na(2)—O distance is $2.36(3)$ Å, considerably shorter than the average Na(1)—O distance. Na(1) and Na(2) share two water O atoms: O(5) and O(6).

In this structure there are eight hydrogen bonds, one associated with each of the eight inequivalent water H atoms. Table 3 lists selected distances and angles associated with these hydrogen bonds. Fig. 3 depicts the hydrogen bonds involving the waters of

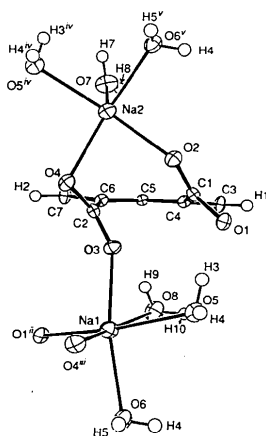


Fig. 2. An ORTEP (Johnson, 1976) view of the sodium ion coordination of the title compound, with our numbering scheme. The direction of view is oriented in the mean plane of the naphthalene core along the C(5)—C(5') bond. Thermal ellipsoids are drawn at 50% probability for all atoms except H for which they have been set artificially small. Note the rotation of the carboxylate groups out of the mean plane of the naphthalene core.

Table 3. Hydrogen-bond parameters (Å, °) for tetrasodium 1,4,5,8-naphthalenetetracarboxylate octahydrate

O—H...A	O...A	H...A	O—H...A
O(5)—H(3)—O(1)	2.900 (3)	1.99 (3)	164 (3)
O(5)—H(4)—O(2 ⁱⁱⁱ)	2.761 (3)	1.98 (3)	174 (3)
O(6)—H(5)—O(3 ⁱⁱⁱ)	2.833 (3)	1.92 (3)	174 (3)
O(6)—H(6)—O(4 ⁱⁱⁱ)	2.790 (3)	1.94 (3)	170 (3)
O(7)—H(7)—O(1 ^{iv})	2.883 (3)	2.08 (3)	155 (3)
O(7)—H(8)—O(8 ⁱ)	2.885 (3)	2.04 (3)	163 (3)
O(8)—H(9)—O(3)	2.831 (3)	2.03 (3)	152 (3)
O(8)—H(10)—O(7 ^{vii})	2.903 (3)	2.02 (3)	164 (3)
Mean	2.848 (50)	2.00 (5)	165 (8)

Symmetry code: (–) x, y, z ; (i) $-x, -y, -z$; (iii) $\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$; (iv) $x, 1 + y, z$; (vi) $-\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$; (vii) $x, -1 + y, z$.

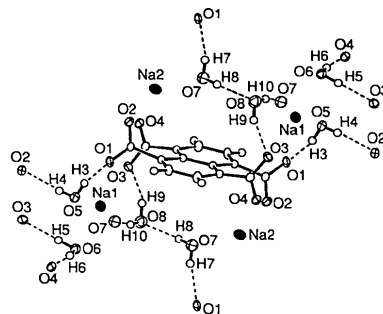


Fig. 3. An ORTEP (Johnson, 1976) view of the title compound depicting the hydrogen bonding (dashed lines). Thermal ellipsoids are drawn at 50% probability for all atoms except H for which they have been set artificially small. The C and H atoms have been drawn with boundary ellipsoids only; the O atoms with boundary and principal axis ellipsoids; the sodium ions have been filled.

hydration associated with one tetrasodium 1,4,5,8-naphthalenetetracarboxylate octahydrate unit. The average H...O (acceptor) distance is $2.00(5)$ Å, the average O...O (acceptor) distance is $2.85(5)$ Å and the average O—H...O (acceptor) angle is $165(8)^\circ$. All of these values are reasonable for hydrogen bonds involving water (see, for example, Ward & Luehrs, 1983). Because of hydrogen bonding, the positions of the water molecules are not optimal with respect to the Na atoms: for example, the positioning of the H(9)—O(8)—H(10) water molecule is such that there are two H atoms whose distances to Na(1) are shorter than the Na(1)—O(8) distance: H(9), $2.51(4)$ Å from Na(1) and H(5), attached to O(6), $2.58(3)$ Å from Na(1), the Na(1)—O(8) distance being $2.656(2)$ Å. This energetically unfavorable arrangement is apparently compensated for by the hydrogen bonding involving the H(9)—O(8)—H(10) water molecule, both as donor though H(9) and H(10), and as acceptor via O(7ⁱ)—H(8ⁱ)...O(8) (see Fig. 3). Two of the four inequivalent water O atoms, O(5) and O(6), are not involved in hydrogen bonding as acceptors. They are, however, coordinated to two Na atoms, such that the angle Na(1)—O(5)—Na(2ⁱⁱⁱ) is $124.1(1)$ and Na(1)—O(6)—Na(2^{xiii}) is $121.3(1)^\circ$.

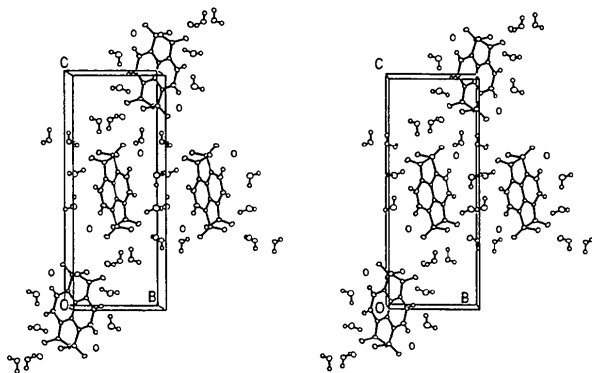


Fig. 4. A unit cell (ORTEP; Johnson, 1976) of the title compound viewed from a direction nearly along the *a* axis. Four entire formula units are shown to illustrate the stacking along the *b* axis.

Fig. 4 is a stereoview of a unit cell for tetrasodium 1,4,5,8-naphthalenetetracarboxylate octahydrate viewed from a direction nearly along the *a* axis. The anions are stacked along the *b* axis and make an angle of 38.6° with the *ac* plane. The separation of corresponding atoms in adjacent anions within the stack is $8.144(3) \text{ \AA}$, the length of the *b* axis. The stacks are staggered such that the carboxyl anions do not line up with each other as they might in their acid forms. The sodium cations, by coordinating with the carboxyl anions, partially occupy the space between the organic portions of the structure, with the water molecules completing the sodium ion coordination polyhedra and filling the remaining space. The $\text{H}_2\text{O}(5)$ and $\text{H}_2\text{O}(6)$ water molecules are positioned between the carboxyl anions while the $\text{H}_2\text{O}(7)$ and $\text{H}_2\text{O}(8)$ water molecules are positioned between the naphthalene cores. The combined effect

of the close approaches, the anion-cation coordination and the hydrogen bonding is to cause the displacement parameters for the atoms in the present study to be significantly smaller than for typical organic structures. The average B_{eq} for the C and O atoms comprising the present structure is $1.4(2) \text{ \AA}^2$; the average B_{eq} for the C and O atoms of 1,8-naphthalenedicarboxylic acid, for example, is $4.1(7) \text{ \AA}^2$ (Fitzgerald, Gallucci & Gerkin, 1991).

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Structure of $[\text{CH}_3\text{TMPP}]_2\text{Co}_2\text{Cl}_6$ [$\text{CH}_3\text{TMPP} = \text{Tris}(2,4,6\text{-trimethoxyphenyl})\text{-methylphosphonium}$]

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Abstract. Tris(2,4,6-trimethoxyphenyl)methylphosphonium hexachlorodicobaltate(II), $2\text{C}_{28}\text{H}_{36}\text{O}_9\text{P}^+ \cdot \text{Co}_2\text{Cl}_6^{2-} \cdot 2\text{CH}_2\text{Cl}_2$ (1), $M_r = 1595.6$, triclinic, $P\bar{1}$, $a = 10.889(5)$, $b = 13.54(6)$, $c = 14.005(5) \text{ \AA}$, $\alpha = 63.45(3)$, $\beta = 83.87(3)$, $\gamma = 78.18(4)^\circ$, $V =$

$1808(2) \text{ \AA}^3$, $Z = 1$, $D_x = 1.465 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$, $\mu = 9.35 \text{ cm}^{-1}$, $F(000) = 822$, $T = 295 \text{ K}$, $R = 0.069$ for 3204 unique reflections with $F_o^2 > 3\sigma(F_o^2)$. The unit cell consists of an edge-sharing bitetrahedral $[\text{Co}_2\text{Cl}_6]^{2-}$ dimer with two (crystallographically related) methylated phosphine counterions, CH_3TMPP^+ , and two interstitial solvent

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