

$S = 1.086$
3903 reflections
245 parameters
H atoms treated by a
mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 0.9976P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction:
SHELXTL
Extinction coefficient:
0.0031 (3)
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

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Dipotassium naphthalene-1,8-dicarboxylate–potassium bicarbonate

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Abstract

The title substance, tripotassium naphthalene-1,8-dicarboxylate bicarbonate, $3K^+ \cdot C_{12}H_6O_4^{2-} \cdot HCO_3^-$, crystallized in the centrosymmetric space group *Pbca*. There is a single hydrogen bond. In it, the O and H atoms are ordered and $O_D \cdots O_A$ is 2.651 (3) Å. There is a single significant intermolecular C—H \cdots O interaction, with $C \cdots O_A = 3.480$ (5) Å. Each potassium ion is coordinated by an irregular polyhedron of O atoms. These three polyhedra contain eight, eight and five members; each O atom is a member of at least two polyhedra. Structural comparisons are made with tetrapotassium naphthalene-1,4,5,8-tetracarboxylate hexahydrate.

Comment

This study of the title compound, (I), follows a study of tetrapotassium, tetrarubidium and tetracesium

Table 1. Selected geometric parameters (Å, °)

Mo—N2	1.7420 (15)	N2—C5	1.456 (2)
Mo—N1	1.7437 (14)	C9—C10	1.459 (2)
Mo—C9	2.1866 (17)	C10—C15	1.412 (2)
Mo—C16	2.1958 (16)	C10—C11	1.412 (2)
Mo—C10	2.4673 (16)	C16—C17	1.488 (2)
N1—C1	1.455 (2)		
N2—Mo—N1	113.64 (7)	N1—Mo—C10	118.71 (6)
N2—Mo—C9	103.17 (7)	C9—Mo—C10	35.89 (6)
N1—Mo—C9	105.75 (7)	C16—Mo—C10	91.92 (6)
N2—Mo—C16	104.01 (7)	C1—N1—Mo	160.00 (12)
N1—Mo—C16	102.82 (6)	C5—N2—Mo	162.83 (12)
C9—Mo—C16	127.77 (6)	C10—C9—Mo	82.61 (10)
N2—Mo—C10	119.65 (6)	C9—C10—Mo	81.50 (9)

H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds), and with U_{iso} constrained to be 1.2 (1.5 for methyl and methylene groups) times U_{eq} of the carrier atom, except for those of the benzyl CH₂ groups, the positions of which were refined freely.

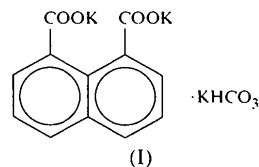
Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1081). Services for accessing these data are described at the back of the journal.

References

- Bell, A., Clegg, W., Dyer, P. W., Elsegood, M. R. J., Gibson, V. C. & Marshall, E. L. (1994a). *J. Chem. Soc. Chem. Commun.* pp. 2247–2248.
- Bell, A., Clegg, W., Dyer, P. W., Elsegood, M. R. J., Gibson, V. C. & Marshall, E. L. (1994b). *J. Chem. Soc. Chem. Commun.* pp. 2547–2548.
- Clegg, W. (1981). *Acta Cryst.* **A37**, 22–28.
- Coles, M. P., Dalby, C. I., Gibson, V. C., Clegg, W. & Elsegood, M. R. J. (1995). *J. Chem. Soc. Chem. Commun.* pp. 1709–1711.
- Coles, M. P. & Gibson, V. C. (1994). *Polym. Bull.* **33**, 529–533.
- Coles, M. P., Gibson, V. C., Clegg, W. & Elsegood, M. R. J. (1998). *Polyhedron*, **17**, 2483–2489.
- Coles, M. P., Gibson, V. C., Clegg, W., Elsegood, M. R. J. & Porrelli, P. A. (1996). *J. Chem. Soc. Chem. Commun.* pp. 1963–1964.
- Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
- Gibson, V. C., Marshall, E. L., Redshaw, C., Clegg, W. & Elsegood, M. R. J. (1996). *J. Chem. Soc. Dalton Trans.* pp. 4197–4199.
- Sheldrick, G. M. (1994). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Stoe & Cie (1988). *DIF4. Diffractometer Control Program*. Version 7.04. Stoe & Cie, Darmstadt, Germany.



naphthalene-1,4,5,8-tetracarboxylate hexahydrates (Fitzgerald *et al.*, 1993) in a series on hydrogen bonding in organic solids. The title compound crystallized in the centrosymmetric space group *Pbca* with one dipotassium naphthalene-1,8-dicarboxylate and one potassium bicarbonate in the asymmetric unit. The refined asymmetric unit, with our numbering scheme, is shown in Fig. 1. In the single hydrogen bond, $O6 \cdots H8 \cdots O2^{vii}$ [symmetry code: (vii) $-\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$], the O and H atoms are ordered, with $O \cdots H = 1.00$ (5), $H \cdots O = 1.68$ (5) and $O_D \cdots O_A = 2.651$ (3) Å, and with $O \cdots H \cdots O = 165$ (5)°. In addition, there is a single significant intermolecular C—H \cdots O interaction, $C2 \cdots H2 \cdots O3^{viii}$ [symmetry code: (viii) $-\frac{1}{2} + x, y, \frac{3}{2} - z$], which has $H \cdots O = 2.50$, $C \cdots O = 3.480$ (5) Å and $C \cdots H \cdots O = 176$ ° (no s.u.'s are given for quantities involv-

ing H2 since it is fixed). The first-level graph (Bernstein *et al.*, 1995) for the hydrogen bond is finite, with descriptor $D(3)$, while that for the C—H···O interaction is a chain, with descriptor $C(7)$, which propagates along **a**. The basic second-level graph (involving both these interactions) is also finite, with descriptor $D_3^3(16)$, and there are, of course, no higher-level graphs.

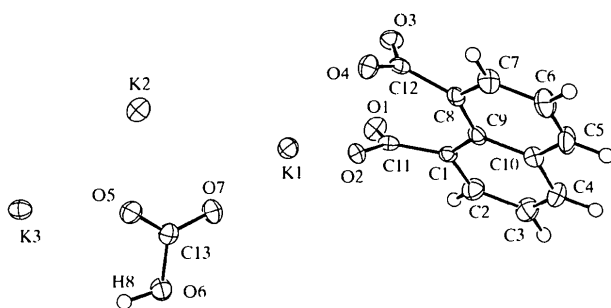


Fig. 1. ORTEP (Johnson, 1976) drawing of (I), showing our numbering scheme. Displacement ellipsoids are drawn for 50% probability for all non-H atoms; spheres of arbitrary small radii depict H atoms.

The absence of further significant C—H···O interactions is undoubtedly principally a consequence of the formation of three cation oxo complexes. Cations K1 and K2 are coordinated by eight O atoms, while K3 is coordinated by five O atoms, all in irregular polyhedrons. The K···O distances range from 2.736 (3) to 3.050 (3) Å for K1, from 2.710 (3) to 3.224 (3) Å for K2 and from 2.606 (3) to 2.767 (3) Å for K3. (A listing of individual distances and angles in these polyhedra is given in the deposited material.) For comparison, in tetrapotassium naphthalene-1,4,5,8-tetracarboxylate hexahydrate (hereafter TNTH; Fitzgerald *et al.*, 1993), there are two inequivalent potassium ions, and each is coordinated by seven O atoms in an irregular polyhedron. The K···O distances in TNTH range from 2.657 (2) to 3.278 (2) Å. Thus, the K···O distances are quite similar in these two cases. In TNTH, the origins of the coordinating O atoms are: 6-carboxylate, 1-water for K1 and 4-carboxylate, 3-water for K2. In (I), the origins of the coordinating O atoms are: 3-carboxylate, 5-bicarbonate for K1; 4-carboxylate, 4-bicarbonate for K2; and 4-carboxylate, 1-bicarbonate for K3. All O atoms in (I) participate in at least two of these complexes, while two participate in all three.

The naphthalene core of (I) is nearly planar, the maximum deviation of any of its atoms from the best-fit plane describing them being 0.017 (4) Å, while the average deviation is 0.008 (2) Å. The dihedral angle between the best-fit core plane and the carboxylate group plane is 53.8 (4)° for the C11/O1/O2 group and 56.0 (4)° for the C12/O3/O4 group. These values are

very similar to the values between the naphthalene core plane and the two inequivalent carboxylate-group planes of TNTH, 52.7 (1) and 52.4 (1)°. In (I), the carboxylate-group C atoms lie on opposite sides of the naphthalene core plane, 0.218 (4) and 0.140 (4) Å from it; in TNTH, the disposition is qualitatively the same, but the distances are larger, 0.392 (2) and 0.409 (2) Å. As expected, the naphthalene core angles in (I) show a pattern of values typical of 1,8-substituted naphthalenes (see *e.g.* Fitzgerald *et al.*, 1991); thus, for example, C1—C9—C8 measures 125.6 (3)°, while C4—C10—C5 measures 120.0 (4)°, and C9—C1—C11 and C9—C8—C12 measure 125.0 (3) and 124.6 (3)°, respectively. The bicarbonate anion, including H8, is very nearly planar, the maximum deviation of any atom from the best-fit plane being less than the s.u. of that deviation, and with $\chi^2 = 1.0$.

Selected bond distances and angles are given in Table 1. All distances and angles fall within normal ranges. The closest intermolecular approaches, excluding pairs of atoms involved in the hydrogen bond and C—H···O interactions discussed above, are not significantly less than the corresponding Bondi (1964) van der Waals radius sum. A packing diagram is presented as Fig. 2.

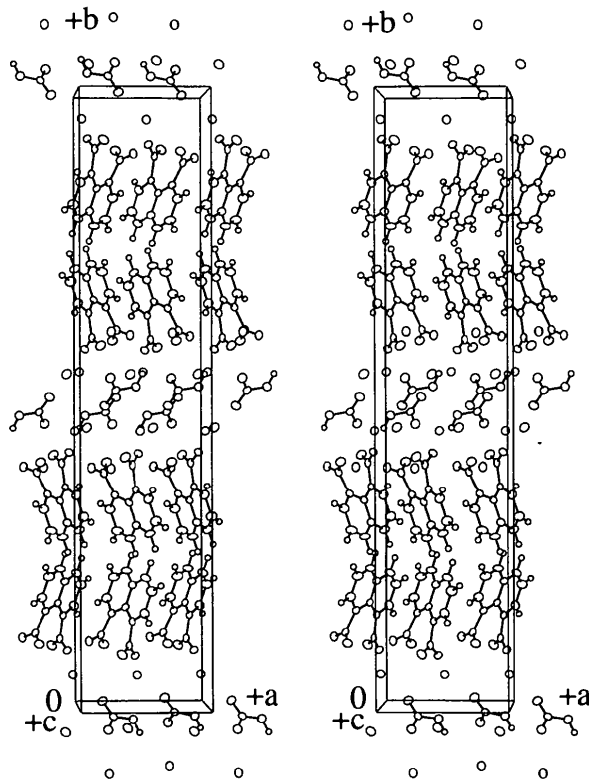


Fig. 2. ORTEP (Johnson, 1976) packing stereodiagram of (I). Displacement ellipsoids are drawn for 50% probability for all non-H atoms; spheres of arbitrary small radii depict H atoms.

Experimental

The title compound was obtained by treating 1,8-naphthalic anhydride from the Aldrich Chemical Company with excess aqueous KOH, followed by slow evaporation. During evaporation, CO₂ was absorbed from the ambient air to form the KHCO₃ which cocrystallized with the organic salt. The title crystals occurred as somewhat fragile thin plates. One such crystal, uncut, constituted the experimental sample.

Crystal data

3K ⁺ ·C ₁₂ H ₆ O ₄ ²⁻ ·HCO ₃ ⁻	Mo K α radiation
$M_r = 392.49$	$\lambda = 0.71073 \text{ \AA}$
Orthorhombic	Cell parameters from 25 reflections
<i>Pbca</i>	$\theta = 13.4\text{--}14.9^\circ$
$a = 7.937 (3) \text{ \AA}$	$\mu = 0.97 \text{ mm}^{-1}$
$b = 37.789 (4) \text{ \AA}$	$T = 296 \text{ K}$
$c = 9.696 (3) \text{ \AA}$	Uncut plate
$V = 2908 (1) \text{ \AA}^3$	$0.27 \times 0.23 \times 0.12 \text{ mm}$
$Z = 8$	Colorless
$D_x = 1.793 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

AFC-5S diffractometer	$\theta_{\max} = 27.5^\circ$
ω scans	$h = 0 \rightarrow 10$
Absorption correction:	$k = 0 \rightarrow 49$
empirical ψ scan (North <i>et al.</i> , 1968)	$l = -12 \rightarrow 0$
$T_{\min} = 0.788$, $T_{\max} = 0.890$	6 standard reflections
3348 measured reflections	every 150 reflections
3348 independent reflections	intensity variation: $\pm 3.4\%$
1980 reflections with $I > 2\sigma I$	(average maximum relative intensity)

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.001$
$R(F) = 0.044$	$\Delta\rho_{\max} = 1.01 \text{ e \AA}^{-3}$
$wR(F^2) = 0.074$	$\Delta\rho_{\min} = -0.97 \text{ e \AA}^{-3}$
$S = 1.35$	Extinction correction: none
3348 reflections	Scattering factors from
212 parameters	Stewart <i>et al.</i> (1965) for
H atoms: see below	H and Creagh & McAuley
$w = 1/\sigma^2(F^2)$	(1992) for C, O, K
where $\sigma^2 = \sigma_{\text{cs}}^2$	
+ $(0.003I)^2$	

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—C11	1.255 (4)	O5—C13	1.254 (4)
O2—C11	1.265 (4)	O6—C13	1.371 (4)
O3—C12	1.257 (4)	O7—C13	1.245 (4)
O4—C12	1.248 (4)		
O1—C11—O2	125.6 (3)	O4—C12—C8	117.1 (3)
O1—C11—C1	118.3 (3)	O5—C13—O6	117.9 (3)
O2—C11—C1	115.9 (3)	O5—C13—O7	127.7 (4)
O3—C12—O4	126.3 (4)	O6—C13—O7	114.4 (3)
O3—C12—C8	116.5 (3)		

Scan widths were $(1.00 + 0.35\tan\theta)^\circ$ in ω , with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and centrosymmetric intensity statistics indicated a non-standard setting of space group No. 61. Prior to

refinement, the cell and data were transformed to the standard setting *Pbca*; since refinement proceeded well, it was adopted. Difference Fourier methods were used to locate initial H-atom positions, which were refined isotropically; refined C—H distances ranged from 0.88 to 0.96 \AA . Subsequently, the ring H atoms were made canonical with C—H = 0.98 \AA and $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the attached C atom. The refined O—H distance is 1.00 (5) \AA . In late stages of refinement, the predicted extinction coefficient was negative, and extinction was not included in the model. The maximum positive residual density peak is located $\sim 0.05 \text{ \AA}$ from $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, a center of symmetry; the maximum negative peak is located $\sim 0.9 \text{ \AA}$ from K1. With respect to the larger-than-normal residual densities, we note that an F^2 refinement excluding only data having $I < 0.1\sigma_I$ and carried to a maximum shift-to-error ratio of 0.001 is characterized by 2666 independent observations and 212 variables (ratio = 12.6), $S = 1.29$, $wR(F^2) = 0.063$, and peak residual densities of +0.66 and -0.64 e \AA^{-3} . These results demonstrate that the weakest data contribute preferentially to the peak residual densities when no data are excluded. This is virtually certainly due to the close spacing of some reflections (partial overlapping of adjacent reflections with the background regions of a given weak reflection) produced by the very long b axis.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCR electronic archives (Reference: FR1190). Services for accessing these data are described at the back of the journal.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Creagh, D. C. & McAuley, W. J. (1992). *International Tables for X-ray Crystallography*, Vol. C, pp. 219–222. Dordrecht: Kluwer Academic Publishers.
- Fitzgerald, L. J., Gallucci, J. C. & Gerkin, R. E. (1991). *Acta Cryst.* **B47**, 776–782.
- Fitzgerald, L. J., Gallucci, J. C. & Gerkin, R. E. (1993). *Acta Cryst.* **C49**, 1287–1294.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1988). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

- Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
- Spek, A. L. (1990). *Acta Cryst.* A46, C-34.
- Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* 42, 3174–3187.

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(C₂H₁₀N₂)[Co(H₂O)₆](HPO₄)₂: a supramolecular three-dimensional hydrogen-bonding network

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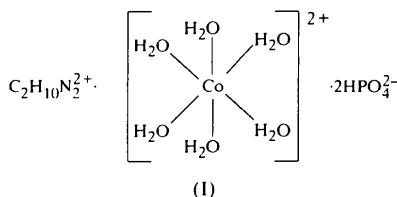
Abstract

The title compound, ethylenediammonium hexaaquacobalt bis(hydrogenphosphate), consists of [Co(H₂O)₆]²⁺ and [enH₂]²⁺ cations (en is ethylenediamine), and [HPO₄]²⁻ anions interconnected by an extensive intermolecular three-dimensional hydrogen-bonding network. The [enH₂]²⁺ cations play an important role in the templating effect. Both [Co(H₂O)₆]²⁺ cations are situated on inversion centers. The average Co—O and P—O bond distances are 2.075 (6) and 1.54 (2) Å, respectively.

Comment

Most crystal-engineering studies have thus far focused on the use of hydrogen bonding between suitable organic molecules for generating multi-dimensional networks (Desiraju, 1995). To a lesser extent, inorganic synthons or a combination of inorganic and organic building blocks capable of intermolecular hydrogen bonding have been explored for their use in solid-state supramolecular chemistry.

The crystal structure of the title compound, ethylenediammonium hexaaquacobalt bis(hydrogenphosphate), (I), is composed of two crystallographically independent exactly centrosymmetric octahedral [Co(H₂O)₆]²⁺



complex cations, both situated on inversion centers, two [HPO₄]²⁻ anions and an [enH₂]²⁺ cation. First of all, the [Co(H₂O)₆]²⁺ cations and [HPO₄]²⁻ anions are linked by hydrogen bonds to form an infinite three-dimensional framework with the [enH₂]²⁺ cation located in the tunnel along the *a* axis. Fig. 1 shows two different views of this supramolecular three-dimensional network with and without the [enH₂]²⁺ cation in the void space. The asymmetric unit that gives rise to the network structure under symmetry expansion is shown in Fig. 2. The N

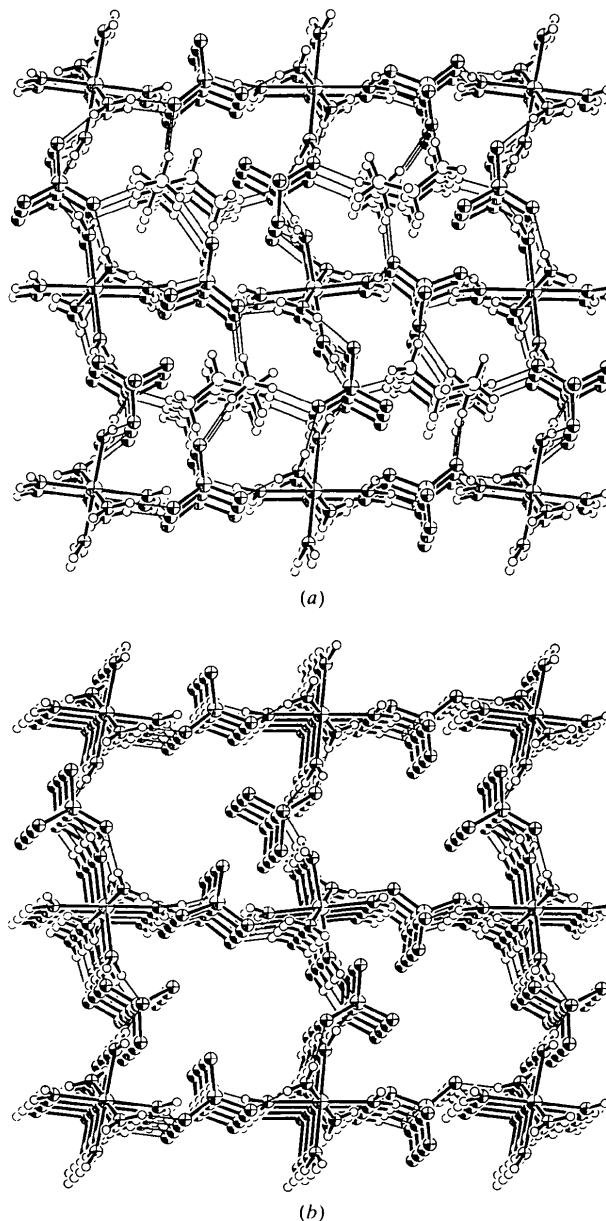


Fig. 1. Projections along the *a* axis of the three-dimensional network formed by the title compound with (a) the [enH₂]²⁺ cations in the void space and (b) the [enH₂]²⁺ cations removed.