Structures of Tetrapotassium, Tetrarubidium and Tetracaesium 1,4,5,8-Naphthalene-tetracarboxylate Hexahydrates

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Abstract

The three title salts are isomorphic except for one structural feature. Each of the two water molecules of the tetrapotassium structure has one H atom disordered over two sites in a cyclic hydrogen-bond arrangement. Disordered H atoms appear not to be present in the tetrarubidium and tetracaesium structures. The effect of cation size on the geometry of the organic anion in these solids is most readily observed in the configuration and conformation of the carb-oxylate groups. The four unique C—O bond lengths, and the four unique C—C—O bond angles, of the carboxylate groups exhibit more than one value and in a consistent manner among the three structures. Additionally, the deviations of the planes of the carboxylate groups with respect to the mean planes of the naphthalene cores change consistently within this series of Group IA salts. The cations are coordi-nated by seven O atoms in irregular polyhedra with the ranges of *M*—O(water) distances being: K 2.657 (2)–3.278 (2), Rb 2.802 (3)–3.255 (3) and Cs 2.982 (3)–3.330 (3) Å. All water H atoms are involved in hydrogen bonds. Mean distances and angles for all three structures are: O···O(acceptor) = 2.79 (3), H···O(acceptor) = 1.87 (6) Å; O—H··· O(acceptor) = 162 (10)°. The molecules are arranged in the crystal in such a manner that the organic anions are surrounded by cations and water mol-ecules, resulting in little direct interaction of the organic portions with one another.

Comment

The structures of the Group IA salts of 1,4,5,8-naphthalenetetracarboxylic acid have been deter-mined as part of a continuing investigation of hydro-gen bonding in the organic solid state. This report presents results for the three title compounds (I) and compares them with those for tetralithium 1,4,5,8-naphthalenetetracarboxylate dodecahydrate (Fitz-gerald, Gallucci & Gerkin, 1992) and tetrasodium 1,4,5,8-naphthalenetetracarboxylate octahydrate

(Fitzgerald, Gallucci & Gerkin, 1991b). Of particular interest in this series is the effect of cation size on crystal structure and the attendant hydrogen-bonding network, as well as on the conformation of the organic anion. Heretofore, no structural series for simple Group IA salts of an aromatic carboxylic acid has been reported. Structures of aromatic acid salts have been reported, and these are compared to the structures of the tetranaphthalate salts. More-over, there have been few reports of hydrated aroma-tic salts in which the H atoms have been located and refined successfully. The present study, therefore, was also planned to add appreciably to the structural data available for hydrated aromatic salts.

(I)
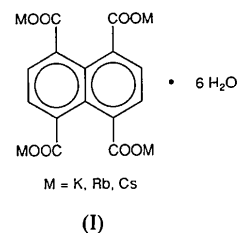
Final atomic coordinates, equivalent isotropic and isotropic displacement parameters and their uncertainties are given in Table 1. The 1,4,5,8-naphthalenetetracarboxylate anion is shown in Fig. 1 with the mean interatomic distances of the three structures studied here specified in one asymmetric unit and the mean angles in the other. Selected
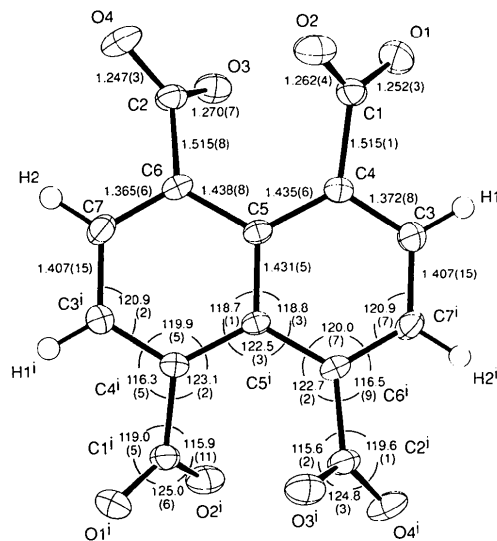

Fig. 1. An *ORTEP*II (Johnson, 1976) view of the 1,4,5,8-naphthalenetetracarboxylate anion, with adopted numbering scheme. Displacement ellipsoids have been drawn at 50% prob-ability for all atoms except H, for which they have been set artificially small. Bond lengths (Å) and angles (°) are mean values for the three independent anions determined in the title structures, with the spread of values given within parentheses.

Table 1. *Final positional parameters and equivalent isotropic and isotropic displacement parameters* (Å²) *with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B
K salt				
K(1)	0.84237 (7)	0.22404 (6)	0.46906 (3)	2.84 (2)
K(2)	0.43019 (7)	0.36756 (7)	0.71571 (5)	3.58 (2)
O(1)	0.7591 (2)	0.5499 (2)	0.6463 (1)	2.82 (5)
O(2)	1.0665 (2)	0.5341 (2)	0.6840 (1)	2.51 (4)
O(3)	0.7988 (2)	0.1513 (2)	0.7027 (1)	2.34 (4)
O(4)	1.0914 (2)	0.1004 (2)	0.6788 (1)	2.89 (4)
O(5)	0.4283 (3)	0.1936 (3)	0.4540 (2)	3.86 (6)
O(6)	0.6172 (3)	0.2562 (4)	1.1378 (2)	4.26 (8)
O(7)	0.5553 (3)	0.1363 (4)	0.8733 (2)	4.14 (7)
C(1)	0.9068 (3)	0.5491 (2)	0.7181 (1)	1.90 (5)
C(2)	0.9756 (3)	0.1720 (2)	0.7419 (1)	1.85 (5)
C(3)	0.8318 (2)	0.7388 (3)	0.9144 (1)	1.91 (5)
C(4)	0.9006 (2)	0.5785 (2)	0.8579 (1)	1.52 (4)
C(5)	0.9854 (2)	0.4652 (2)	0.9326 (1)	1.35 (4)
C(6)	1.0428 (2)	0.2852 (2)	0.8784 (1)	1.57 (4)
C(7)	1.1406 (2)	0.1932 (2)	0.9535 (2)	1.92 (5)
H(51)	0.367 (4)	0.079 (5)	0.406 (3)	5.5 (7)†
H(52)	0.361 (4)	0.270 (5)	0.425 (3)	5.6 (7)†
H(61)	0.716 (5)	0.297 (5)	1.168 (3)	5.5 (9)†
H(71)	0.639 (4)	0.131 (4)	0.833 (3)	4.9 (7)†
H(62)	0.620 (7)	0.237 (7)	1.051 (6)	3 (1)†‡
H(63)	0.580 (10)	0.162 (10)	1.141 (6)	4 (2)†‡
H(72)	0.572 (11)	0.205 (12)	0.938 (8)	7 (2)†‡
H(73)	0.496 (8)	0.016 (10)	0.856 (5)	3 (1)†‡
Rb salt				
Rb(1)	0.83707 (6)	0.21599 (6)	0.46193 (4)	2.81 (2)
Rb(2)	0.42901 (6)	0.37049 (6)	0.71711 (4)	3.39 (2)
O(1)	0.7682 (4)	0.5544 (4)	0.6456 (2)	2.7 (1)
O(2)	1.0684 (4)	0.5260 (4)	0.6904 (2)	2.4 (1)
O(3)	0.7880 (4)	0.1600 (4)	0.7097 (2)	2.3 (1)
O(4)	1.0741 (4)	0.1037 (4)	0.6868 (3)	2.8 (1)
O(5)	0.4081 (6)	0.1839 (6)	0.4476 (4)	4.5 (2)
O(6)	0.6189 (7)	0.2484 (6)	1.1352 (4)	5.0 (2)
O(7)	0.5528 (6)	0.1262 (6)	0.8773 (4)	4.5 (2)
C(1)	0.9111 (5)	0.5466 (5)	0.7198 (3)	1.9 (1)
C(2)	0.9641 (6)	0.1783 (5)	0.7486 (3)	2.0 (1)
C(3)	0.8364 (5)	0.7314 (5)	0.9111 (4)	2.0 (1)
C(4)	0.9017 (5)	0.5748 (5)	0.8569 (3)	1.5 (1)
C(5)	0.9841 (5)	0.4653 (5)	0.9338 (3)	1.4 (1)
C(6)	1.0372 (5)	0.2890 (5)	0.8821 (3)	1.6 (1)
C(7)	1.1337 (5)	0.2022 (6)	0.9592 (3)	2.0 (1)
H(51)	0.347 (10)	0.067 (10)	0.398 (6)	8 (2)†
H(52)	0.357 (8)	0.239 (9)	0.429 (6)	5 (2)†
H(61)	0.730 (9)	0.300 (10)	1.168 (6)	6 (2)†
H(71)	0.626 (8)	0.129 (8)	0.838 (5)	4 (2)†
H(62)	0.622 (10)	0.211 (11)	1.080 (6)	6.0§
H(73)	0.484 (8)	0.013 (9)	0.861 (6)	6.0§
Cs salt				
Cs(1)	0.82874 (3)	0.20586 (3)	0.45298 (2)	2.85 (1)
Cs(2)	0.42928 (3)	0.37318 (4)	0.71770 (3)	3.75 (1)
O(1)	0.7816 (4)	0.5579 (4)	0.6463 (2)	2.88 (8)
O(2)	1.0692 (3)	0.5183 (4)	0.6977 (2)	2.72 (7)
O(3)	0.7825 (3)	0.1655 (3)	0.7158 (2)	2.38 (7)
O(4)	1.0590 (4)	0.1084 (4)	0.6966 (2)	2.95 (8)
O(5)	0.3852 (5)	0.1797 (5)	0.4361 (4)	4.9 (1)
O(6)	0.6228 (5)	0.2489 (6)	1.1271 (4)	5.6 (1)
O(7)	0.5529 (6)	0.1091 (6)	0.8760 (4)	5.3 (1)
C(1)	0.9166 (5)	0.5439 (4)	0.7221 (3)	2.10 (8)
C(2)	0.9552 (4)	0.1838 (4)	0.7550 (3)	1.96 (8)
C(3)	0.8441 (5)	0.7219 (4)	0.9072 (3)	2.3 (1)
C(4)	0.9067 (4)	0.5710 (4)	0.8567 (3)	1.80 (8)
C(5)	0.9839 (4)	0.4658 (4)	0.9348 (2)	1.60 (7)
C(6)	1.0314 (4)	0.2951 (4)	0.8866 (3)	1.79 (7)
C(7)	1.1251 (5)	0.2118 (4)	0.9637 (3)	2.34 (9)
H(51)	0.322 (8)	0.093 (8)	0.396 (5)	5 (1)†
H(52)	0.338 (8)	0.262 (9)	0.398 (6)	5 (1)†
H(61)	0.792 (10)	0.308 (10)	1.164 (7)	9 (2)†

H(62)	0.617 (8)	0.213 (8)	1.044 (6)	5 (1)†
H(71)	0.630 (7)	0.096 (7)	0.825 (5)	3 (1)†
H(73)	0.496 (8)	−0.014 (9)	0.872 (5)	5 (1)†

† Refined isotropically.

‡ Half occupied.

§ Positional parameters refined; B fixed by reference to B_{eq} of attached atom.

Table 2. *Evaluation of the conformation of the 1,4,5,8-naphthalenetetracarboxylate anion in the series of Group IA salts*

Results for the tetralithium salt are from Fitzgerald *et al.* (1992) and for the tetrasodium salt from Fitzgerald *et al.* (1991*b*); other results from present study. E.s.d.'s are given in parentheses.

	Li	Na	K	Rb	Cs
Mean deviation of C atoms comprising naphthalene ring from least-squares plane (Å)					
	0.030	0.028	0.034	0.037	0.042
Distance of atoms from least-squares plane of naphthalene ring (Å)					
C(1)	0.389 (1)	0.334 (2)	0.392 (2)	0.438 (4)	0.459 (3)
O(1)	−0.269	−0.371	−0.278	−0.183	−0.116
O(2)	1.382	1.318	1.388	1.419	1.420
C(2)	−0.371	−0.280	−0.409	−0.431	−0.460
O(3)	−1.387	−1.279	−1.408	−1.438	−1.482
O(4)	0.314	0.512	0.238	0.198	0.151
Dihedral angle between plane of carboxylate group and least-squares plane of naphthalene ring (°)					
C(1)—O(1)—O(2)	52.7 (1)	52.5 (1)	52.7 (1)	51.4 (2)	49.6 (2)
C(2)—O(3)—O(4)	54.6 (1)	55.1 (1)	52.4 (1)	52.8 (2)	53.4 (2)

parameters describing the conformations of each of the carboxylate anions are given in Table 2 along with parameters from two other structures of Group IA salts which have been previously reported. Table 3 lists the hydrogen-bond geometry. Data pertaining to the interatomic distances and angles involved in the coordination polyhedra and to the water-molecule geometry have been deposited.

The three sets of bond lengths and angles for the organic anions in the present study agreed very closely with one another. Consequently, the mean values of the three determinations are shown in Fig. 1, with the spread of the values given within parentheses. The dimensions of the naphthalene core of this mean anion agree well with those from the tetralithium and tetrasodium structures, the same pattern of bond lengths occurring in all cases. The bond angles around C(4) and C(6) deviate from 120° in a manner typical of 1,8-substituted naphthalenes (Fitzgerald, Gallucci & Gerkin, 1991*a*), while the angle at C(5) is smaller than is normally found for 1,8-substituted naphthalenes. This is presumably a consequence of the interaction on both sides of the naphthalene ring for the tetrasubstituted naphthalene. Again, the arrangement is in accord with the results for the tetralithium and tetrasodium structures. The bond lengths and angles of the carboxylate groups in the present study do not show the equal values expected for carboxylate anions. The C—O bond lengths for the C(1) carboxylate group

Table 3. *Hydrogen-bond geometry based on neutron-adjusted* H-*atom positions* (*Antsyshkina et al.*, 1982) *for the title structures*

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

O—H···O	O···O (Å)			H···O (Å)			O—H···O (°)		
	K	Rb	Cs	K	Rb	Cs	K	Rb	Cs
O(5)—H(51)—O(3^{iv})	2.790 (2)	2.778 (5)	2.780 (4)	1.84 (3)	1.82 (7)	1.85 (6)	171 (3)	175 (6)	162 (6)
O(5)—H(52)—O(1^v)	2.786 (2)	2.789 (5)	2.784 (4)	1.83 (4)	1.84 (6)	1.84 (7)	172 (3)	167 (8)	166 (6)
O(6)—H(61)—O(2^{iv})	2.788 (3)	2.799 (5)	2.831 (5)	1.90 (4)	1.92 (6)	2.05 (8)	152 (3)	151 (6)	138 (6)
O(6)—H(62)—O(7)	2.807 (3)	2.774 (6)	2.756 (6)	1.87 (6)	1.86 (7)	1.82 (7)	162 (5)	157 (9)	166 (5)
O(6)—H(63)—O(7^{vii})	2.837 (3)	—	—	1.90 (8)	—	—	172 (7)	—	—
O(7)—H(71)—O(3)	2.725 (2)	2.734 (5)	2.751 (5)	1.80 (3)	1.79 (6)	1.84 (5)	162 (3)	166 (6)	156 (5)
O(7)—H(72)—O(6)	2.807 (3)	—	—	1.95 (9)	—	—	148 (8)	—	—
O(7)—H(73)—O(6^{vii})	2.837 (3)	2.804 (7)	2.804 (6)	1.90 (6)	1.88 (6)	1.85 (6)	165 (5)	163 (6)	175 (5)
	Average = 2.788 (30)			Average = 1.87 (6)			Average = 162 (10)		

Symmetry code: (none) x, y, z; (iv) $1 - x, -y, 1 - z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $2 - x, 1 - y, 2 - z$; (vii) $1 - x, -y, 2 - z$.

exhibit a slight difference of 0.010 Å, while those for the C(2) group differ by 0.023 Å. Both differences are larger than the combined spread of values in each case with the C(2) group exhibiting a more significant difference. In addition, the C—C—O angles are consistent with the difference in lengths: for the C(1) group the angles differ by 3.1° and for the C(2) group by 4.0°. The bond lengths of the carboxylate groups in the tetralithium and tetrasodium structures are more nearly equal and the bond angles of the tetrasodium carboxylate groups differ by no more than 1.0°. Carboxylate anions with differing bond lengths have been reported for dilithium maleate dihydrate (Town & Small, 1973) and calcium terephthalate trihydrate (Matsuzaki & Iitaka, 1972), although the cause of this behavior was not discussed. The trend in the present series for the larger cations to exhibit these differences may indicate that packing constraints have a significant role to play in the configuration of the carboxylate groups of organic salts.

Table 2 displays various parameters relating to the conformation of the organic anions in the present series of Group IA salts. In each of the five structures studied, the best least-squares plane was determined for the ten atoms comprising the respective naphthalene cores, along with the mean deviation of the naphthalene core atoms from the least-squares plane. The mean deviation values are listed in Table 2. The values are similar, showing a small but consistent trend such that Cs > Rb > K > Li > Na. A similar trend is evident in the positions, with respect to the naphthalene core, of carboxyl atoms C(1) and C(2) (see Table 2 and Fig. 2): the tetracaesium structure exhibits the largest deviation and the tetrasodium the smallest. For the most part, the carboxyl O atoms are consistent with this trend, as might be expected, with O(1) and O(4) moving closer to the least-squares plane of the naphthalene ring, and O(2) and O(3) moving farther away as the series progresses in the manner described above. It is of interest to note that the two shorter C—O bonds

involve the O atoms closest to the naphthalene ring: O(1) and O(4), and that the two longer C—O bonds involve the O atoms farthest from the naphthalene ring: O(2) and O(3). The effect of the various cations on the conformation of the tetracarboxylate anion parallels the cation size, except for lithium which appears to have an effect larger than would be predicted from size alone. Table 2 also lists the dihedral angles which the respective carboxyl group planes form with the least-squares planes of the naphthalene rings: the C(1)—O(1)—O(2) carboxyl group angle ranges from 49.6 to 52.7° for the five structures while the C(2)—O(2)—O(3) carboxyl group angle ranges from 52.4 to 55.1°. No trends are apparent.
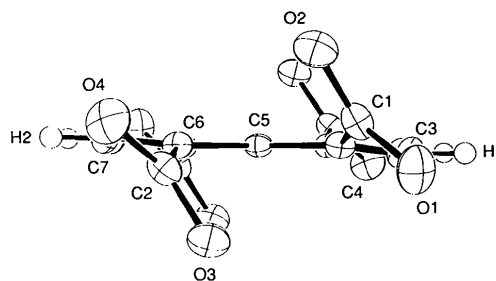

Fig. 2. An *ORTEP*II (Johnson, 1976) view of the organic anion from a direction lying in the plane of the naphthalene rings and along the C(5)—C(5^i) bond. Displacement ellipsoids have been drawn at 50% probability for all atoms except H, for which they have been set artificially small.

The cation coordination for the three title salts is shown in Fig. 3. With a center of inversion at the midpoint of the C(5)—C(5^i) bond there are two inequivalent cations in each case. Cation (1) is coordinated by seven O atoms: six carboxylate O atoms and one water O. The ranges of cation(1)–oxygen distances are: K(1) 2.657 (2)–3.133 (2), Rb(1) 2.802 (3)–3.183 (3), Cs(1) 2.982 (3)–3.305 (3) Å. Cation (2) is also coordinated to seven O atoms: four

carboxylate and three water O atoms. The ranges of cation (2)–oxygen distances are: K(2) 2.760 (2)–3.278 (2), Rb(2) 2.906 (3)–3.255 (3), Cs(2) 3.073 (3)–3.330 (3) Å. These ranges are comparable to those for the respective salts of *o*-sulfobenzoic acid (Teplova, Turskaya, Shibanova, Nekrasov & Belikova, 1986; Teplova, Turskaya, Tovbis, Zavodnik, Shibanova & Belikova, 1984; Sorokina, Molchanov, Turskaya, Furmanova & Belikova, 1989) and of those for the acid phthalate salts (Okaya, 1965; Smith, 1975*a,b*). For each structure in the present study, the cation–carboxylate O distances cover a broader range than the cation–water O distances, with no other trends apparent. The coordination geometries are best described as irregular polyhedra. For each structure, the two cations share three O atoms: O(1), O(3) and O(5). A table of selected distances and angles in these polyhedra has been deposited.
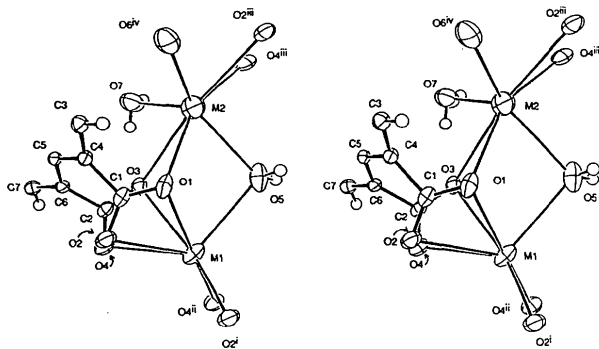
Fig. 3. A stereoview of the metal-ion coordination for the three isomorphic title salts, drawn using *ORTEP*II (Johnson, 1976). Displacement ellipsoids have been drawn at 50% probability for all atoms except H for which they have been set artificially small. For the three structures of this report *M* represents K$^+$, Rb$^+$ or Cs$^+$.

For the water molecules in the three title structures, the mean O—H distance is 0.84 (14) Å and the mean H—O—H angle 106 (7)°, based on the refined H-atom positions. In the tetrapotassium structure, both water molecules [O(6) and O(7)] which occupy positions between naphthalene rings of adjacent anions have one of their H atoms disordered over two sites. The disordered hydrogen sites are positioned in a cyclic arrangement with respect to inversion-related O(6) and O(7) such that each is involved in a hydrogen bond (see Fig. 4). In addition, the refined positions of the half-occupied H atoms produce reasonable water-molecule geometry. The investigation of the H-atom positions for O(6) and O(7) in the tetrarubidium and tetracaesium structures was not as definitive as in the tetrapotassium structure presumably due to the larger

residual electron densities. However, the available evidence indicates that the H atoms in these structures are not disordered. The tetralithium and tetrasodium structures have water molecules that occupy positions between adjacent anions in a similar manner to O(6) and O(7) here, but no evidence of disordered H atoms was found. The disordered arrangement in the potassium structure, therefore, appears to be unique within this series of Group IA salts.
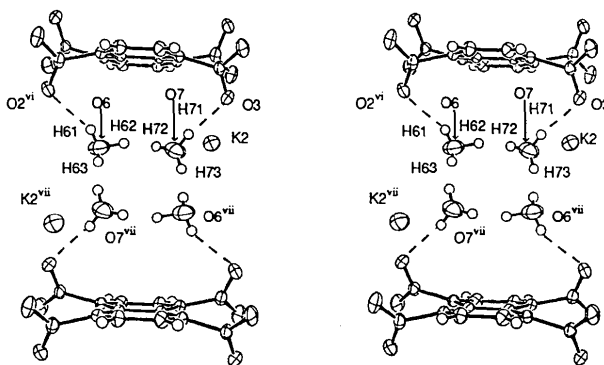

Fig. 4. A stereoview (*ORTEP*II; Johnson, 1976) of a region between adjacent organic anions in the tetrapotassium structure. Water molecules which have disordered H atoms [H(62), H(63), H(72) and H(73)] are displayed. Dashed lines represent hydrogen bonds of ordered H atoms H(61) and H(71). Symmetry code: (none) *x, y, z*; (vii) 1 − *x*, −*y*, 2 − *z*.

The H-atom positions for the three structures reported here were adjusted, based upon neutron diffraction results (Antsyshkina, Dikareva, Porai-Koshits, Fykin, Dudarev & Gusejnov, 1982), to a distance of 0.96 Å from their respective O atoms along the line connecting the refined O- and H-atom positions. These neutron-adjusted hydrogen-bond parameters are listed in Table 3 and have mean values as follows: O···O 2.79 (3), H···O 1.87 (6) Å, O—H···O 162 (10)°. These values are similar to those for the tetralithium and tetrasodium structures as well as to those of other hydrated aromatic carboxylate salts (see, for example, Gougoutas, Ojala & Miller, 1980).

A unit-cell drawing of the tetrapotassium structure is shown in Fig. 5. Except for the disordered H atoms on O(6) and O(7), this represents the structure for the tetrarubidium and tetracaesium cases as well. In these structures, the cations and water molecules separate the adjacent carboxylate groups. In addition, alternating organic and ionic regions are formed along the *x* direction by the positioning of the cations and water molecules between the organic anions. In effect, the organic anions are surrounded by the cations and water molecules, with the associated ionic and hydrogen bonds connecting the

structure in a three-dimensional network. The tetra-lithium and tetrasodium structures are similar to the title structures in that the organic anions also are surrounded by atoms and water molecules, with concomitant three-dimensional networks of ionic and hydrogen bonds. The positioning of the cations with respect to the organic anions is different for these groups as are the numbers of waters of hydration. The lithium structure, with the smallest cation, has twelve waters of hydration and the sodium structure has eight, whereas the three isomorphic title structures have six.
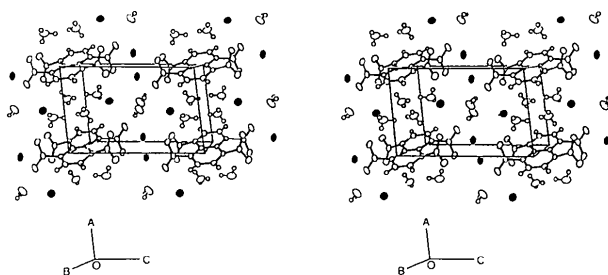
Fig. 5. A unit-cell drawing (ORTEPII; Johnson, 1976) of tetra-potassium 1,4,5,8-naphthalenetetracarboxylate hexahydrate; four complete molecules are shown. Unit-cell drawings for the tetrarubidium and tetracaesium structures are indistinguishable from the structure shown, except that the tetrapotassium structure contains disordered H atoms for O(6) and O(7).

Although the structures of the Li (Gonschorek & Küppers, 1975), Na (Smith, 1975a), K (Okaya, 1965) and Rb (Smith, 1975b) salts of hydrogen phthalate have been reported, as have the structures of the K (Teplova et al., 1986), Rb (Teplova et al., 1984) and Cs (Sorokina et al., 1989) salts of o-sulfobenzoic acids,* no series of simple salts of Group IA cations of an aromatic acid has previously been reported. Although those series are both composed of structures that are acid salts, comparisons with the structures in the present series are instructive. The hydrogen phthalate series has an increasing amount of water of hydration with decreasing size of cation as in the present series. Both anions in the hydrogen phthalate and the o-sulfobenzoic acid structures have their hydrophilic portions on one side of the aromatic ring. Consequently, the structures of their salts are characterized by hydrophobic regions within which the aromatic rings interact, along with hydrophilic regions containing the cations and water molecules, if any. In contrast, the naphthalenetetra-carboxylate anion has hydrophilic groups on both

sides of the aromatic ring system; as a consequence, the cations and water molecules surround the organic anion in such a way that there is no significant direct interaction between the aromatic rings. Finally, neither the K, Rb, Cs salts of hydrogen phthalate nor the respective salts of o-sulfobenzoic acid have isomorphic structures, whereas these naphthalenetetracarboxylate salts have isomorphic structures.
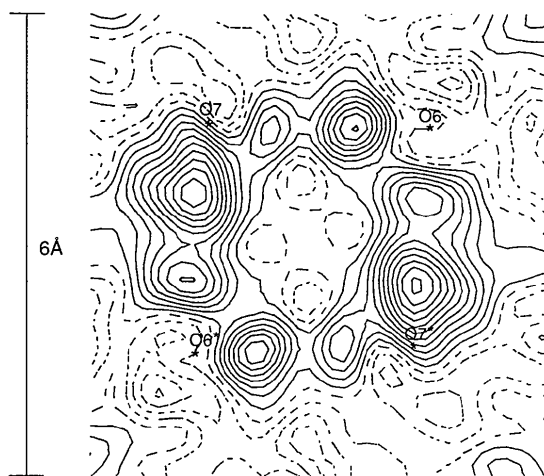

Fig. 6. Fourier difference map of the region near the plane defined by O(6), O(7), O(6^{vii}) and O(7^{vii}) in the tetrapotassium structure. The map was calculated after all atoms, except for H(62), H(63), H(72) and H(73), had been assigned. Symmetry code: (none) x, y, z; (vii) $1 - x, - y, 2 - z$. Solid lines indicate positive electron density; dashed lines indicate zero and negative electron density. The contour interval is 0.04 e Å^{-3}.

* Certain aspects of the structure of caesium hydrogen phthalate are discussed by Sorokina et al. (1989), based on a private communication from T. B. Teplova, T. A. Shibanova and V. N. Molchanov.

Experimental

K salt

Crystal data

K$_4$(C$_{14}$H$_4$O$_8$).6H$_2$O	Mo K$\overline{\alpha}$ radiation
M_r = 564.69	λ = 0.71073 Å
Triclinic	Cell parameters from 25
$P\overline{1}$	reflections
a = 7.189 (1) Å	θ = 13–15°
b = 7.125 (2) Å	μ = 0.894 mm^{-1}
c = 11.034 (2) Å	T = 295 K
α = 103.16 (2)°	Plate
β = 96.74 (2)°	0.38 × 0.35 × 0.15 mm
γ = 99.41 (2)°	Colorless
V = 535.9 (2) Å^3	Crystal source: slow evapo-
Z = 1	ration of aqueous solution
D_x = 1.75 Mg m^{-3}	at room temperature
D_m = 1.76 Mg m^{-3}	

Data collection

Rigaku AFC-5S diffractometer	R_{int} = 0.009
	θ_{max} = 30.0°

ω–2θ scans
Absorption correction:
  empirical
  T_{min} = 0.777, T_{max} = 1.000
3347 measured reflections
3118 independent reflections
2422 observed reflections
  [$I>3\sigma(I)$]

Refinement

Refinement on F
Final R = 0.034
wR = 0.043
S = 1.71
2422 reflections
186 parameters
All H-atom parameters refined
$w = \sigma_F^{-2}$
$(\Delta/\sigma)_{max}$ <0.01

h = 0 → 10
k = −15 → 15
l = −10 → 10
6 standard reflections
  monitored every 150
  reflections
  intensity variation: ±4.0%

$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}
Extinction correction:
  Zachariasen (1967)
Extinction coefficient:
  7.05 (16)×10^{-5}
Atomic scattering factors from Cromer & Waber (1974) (non-H atoms); Stewart, Davidson & Simpson (1965) (H atoms)

Rb salt

Crystal data

Rb$_4$(C$_{14}$H$_4$O$_8$).6H$_2$O
M_r = 750.15
Triclinic
$P\bar{1}$
a = 7.280 (1) Å
b = 7.378 (1) Å
c = 11.179 (1) Å
α = 102.54 (1)°
β = 98.15 (1)°
γ = 99.51 (1)°
V = 568.1 (1) Å^3
Z = 1
D_x = 2.19 Mg m^{-3}
D_m = 2.21 Mg m^{-3}

Mo $K\overline{\alpha}$ radiation
λ = 0.71073 Å
Cell parameters from 25
  reflections
θ = 14.5–15°
μ = 8.396 mm^{-1}
T = 295 K
Column
0.35 × 0.19 × 0.12 mm
Colorless
Crystal source: slow evaporation of aqueous solution at room temperature

Data collection

Rigaku AFC-5S diffractometer
ω–2θ scans
Absorption correction:
  empirical
  T_{min} = 0.587, T_{max} = 1.000
3561 measured reflections
3324 independent reflections
2008 observed reflections
  [$I>3\sigma(I)$]

R_{int} = 0.025
θ_{max} = 30°
h = 0 → 10
k = −15 → 15
l = −10 → 10
6 standard reflections
  monitored every 150
  reflections
  intensity variation: ±2.9%

Refinement

Refinement on F
Final R = 0.032
wR = 0.033
S = 1.15

$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}
Extinction correction:
  Zachariasen (1967)

2008 reflections
176 parameters
All H-atom parameters refined
$w = \sigma_F^{-2}$
$(\Delta/\sigma)_{max}$ <0.01

Extinction coefficient:
  8.8 (3)×10^{-6}
Atomic scattering factors from Cromer & Waber (1974) (non-H atoms); Stewart et al. (1965) (H atoms)

Cs salt

Crystal data

Cs$_4$(C$_{14}$H$_4$O$_8$).6H$_2$O
M_r = 939.91
Triclinic
$P\bar{1}$
a = 7.517 (1) Å
b = 7.637 (2) Å
c = 11.355 (1) Å
α = 101.84 (3)°
β = 99.53 (1)°
γ = 100.40 (1)°
V = 613.6 (4) Å^3
Z = 1
D_x = 2.54 Mg m^{-3}
D_m = 2.54 Mg m^{-3}

Mo $K\overline{\alpha}$ radiation
λ = 0.71073 Å
Cell parameters from 25
  reflections
θ = 14.5–15°
μ = 5.913 mm^{-1}
T = 295 K
Column
0.35 × 0.21 × 0.19 mm
Colorless
Crystal source: slow evaporation of aqueous solution at room temperature

Data collection

Rigaku AFC-5S diffractometer
ω–2θ scans
Absorption correction:
  empirical
  T_{min} = 0.648, T_{max} = 1.000
3833 measured reflections
3584 independent reflections
3157 observed reflections
  [$I>3\sigma(I)$]

R_{int} = 0.014
θ_{max} = 30°
h = 0 → 10
k = −15 → 15
l = −10 → 10
6 standard reflections
  monitored every 150
  reflections
  intensity variation: ±3.5%

Refinement

Refinement on F
Final R = 0.029
wR = 0.039
S = 1.83
3157 reflections
178 parameters
All H-atom parameters refined
$w = \sigma_F^{-2}$
$(\Delta/\sigma)_{max}$ <0.01

$\Delta\rho_{max}$ = 1.22 e Å^{-3}
$\Delta\rho_{min}$ = −1.28 e Å^{-3}
Extinction correction:
  Zachariasen (1967)
Extinction coefficient:
  1.67 (3)×10^{-5}
Atomic scattering factors from Cromer & Waber (1974) (non-H atoms); Stewart et al. (1965) (H atoms)

1,4,5,8-Naphthalenetetracarboxylic acid (Aldrich Chemical Company) was suspended in water and reacted with an excess of the respective Group IA hydroxide. The resulting solutions were mixed with Norit-A decolorizing carbon and filtered. Each salt was then crystallized by slow evaporation of water at room temperature to provide the experimental samples. These were mounted on glass fibers with epoxy cement and coated with Apiezon L grease. Data were collected using graphite-monochromated radiation and a background/scan time-ratio of 0.5. Scan widths were (1.30 + 0.35tanθ), (1.20 + 0.35tanθ) and

$(1.60 + 0.35\tan\theta)°$ for the K, Rb and Cs salts, respectively. A variance was assigned to each reflection by means of the formula $\sigma_I^2 = \sigma_{cs}^2(I) + (0.03I)^2$ in which σ_{cs} is based on counting statistics and I is the integrated intensity. No corrections were made for decay; the data were corrected for Lorentz and polarization effects. ψ-scan absorption corrections (North, Phillips & Mathews, 1968) were applied based on ψ-scan data obtained near the end of each data collection.

Intensity statistics indicated a centrosymmetric space group for each data set; $P\bar{1}$ was consequently given initial preference and since refinement proceeded well it was adopted in each case. The direct-methods program SHELXS86 (Sheldrick, 1985) was used to generate an E map for the tetrapotassium data set and from this the initial positions of the K atoms and the non-H atoms of the naphthalate anion were identified. Fourier difference methods were used to locate the water O atoms and all H-atom positions. For the tetrarubidium and tetracaesium data sets, the positions of the respective cations were determined from Patterson maps and the positions of all remaining atoms were determined by Fourier difference methods. A center of inversion was located at the midpoint of the $C(5)$—$C(5^i)$ bond in each anion; thus each asymmetric unit is one half of the molecular formula. Full-matrix least-squares refinement was performed (TEXSAN; Molecular Structure Corporation, 1989) to minimize the function $\Sigma\sigma_F^{-2}(|F_o| - |F_c|)^2$ in which $\sigma_F = \sigma_I/2FLp$. Non-H atoms were refined anisotropically, H atoms isotropically except as specified below.

In the developing model of the structure of tetrapotassium 1,4,5,8-naphthalenetetracarboxylate, four of the six inequivalent water H atoms [two for O(5), one for O(6) and one for O(7)] were found at positions suitable for hydrogen bonds to carboxylate O atoms and their refinement proceeded normally. However, after assignment of these four H atoms, examination of the Fourier difference map in the region near O(6) and O(7) (Fig. 6) clearly indicated four chemically reasonable positions for the remaining two H atoms. The positions found were in a cyclic arrangement when considered together with inversion-related O(6) and O(7). In addition, each of these positions allowed acceptable hydrogen bonds with one of the water O atoms in the closed loop arrangement. Therefore, four H atoms [H(62), H(63), H(72), H(73)], each having an occupancy factor of 0.5, were placed at the positions indicated by the Fourier difference map. The positions and displacement parameters converged. This model was then compared, using Hamilton's ratio test (Hamilton, 1965), to a model in which the final two water H atoms were treated as fully occupied H atoms, one for O(6) and one for O(7). The half-occupancy hydrogen model was found to be a statistically significant improvement at the 0.005 level.

Refinement of the tetrarubidium and tetracaesium data sets indicated that these structures were isomorphic with that of tetrapotassium, except for the disordered H atoms. The Fourier difference maps of the region near O(6) and O(7) for the tetrarubidium and tetracaesium structures were not as easily interpreted as in the tetrapotassium case. Refinement of half-occupied H atoms did not converge in either case, while refinement of fully occupied H atoms proceeded with some difficulty. The displacement parameters of fully occupied H positions in the tetrarubidium data set had to be fixed at 1.5 times the corresponding values for the O atoms to which they were attached in order for refinement to converge. For the tetracaesium structure the refinement of the fully occupied H positions resulted in an unreasonably large $O(6)$—$H(61)$ bond length of 1.24 Å. Because of these dif-

ficulties, the question of disordered H atoms in the tetrarubidium and tetracaesium structures cannot be resolved definitively. However, the present results indicate that there is no H disorder in these structures, in contrast to the tetrapotassium structure.

For each of the data sets, the unit cell, hkl indices and fractional coordinates were transformed from the order in which they were collected and refined in order that they could more easily be compared: for the K salt $h,k,l \rightarrow -h,-l,-k$; for the Rb and the Cs salts, $h,k,l \rightarrow l,h,k$. All discussion of experimental details refers to the unit cells and data sets prior to transformation; the reported unit cells and fractional coordinates are those after the transformation. The secondary-extinction coefficient was treated as a refined parameter in each case (Zachariasen, 1967); the largest effects were 31.4% of F_o for 013 in the K salt, 28.0% of F_o for 112 in the Rb salt and 42.4% of F_o for 112 in the Cs salt.

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catena-Poly[silver(I)-μ-(cyano-C:N)-cis-bis-(2,2'-bipyridine-N,N')copper(II)-μ-(cyano-N:C)] Dicyanoargentate(I) Monohydrate

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Abstract

The structure of the title complex is built up of positively charged zigzag chains running parallel to the b axis with the composition cis[-μ-CN-Cu(bpy)$_2$-μ-NC-Ag-]$^+$ (bpy = 2,2'-bipyridine), isolated [Ag(CN)$_2$]$^-$ anion and non-coordinated water molecule. The Cu atom is coordinated in the form of a very deformed tetragonal bipyramid (4 + 1 + 1) with unequal distortion of the axial bonds [2.239 (4) and 2.676 (5) Å]. Three crystallographically independent Ag atoms are coordinated linearly by two cyano groups and they are placed along the b axis forming an infinite chain with short Ag···Ag distances

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[3.0439 (4) and 2.9866 (4) Å]. One of the two non-coordinated independent water molecules shows partial occupancy of its disordered position.

Comment

The structure determination of the title complex forms a continuation of the study on the preparation, structure, thermal and other properties of bimetallic dicyanoargentates with nitrogen-containing ligands (Kappenstein, Ouali, Guerin, Černák & Chomič, 1988; Chomič, Černák, Potočňák, Zvereva & Saveljeva, 1993).

From a chemical point of view, two features of the studied structure are outstanding: the coordination mode of the Cu^{II} atom and the existence of infinite chains of Ag atoms with short Ag···Ag distances.

The coordination number of the Cu^{II} atom is six in the form 4 + 1 + 1. Four N atoms (three from bpy and one from a bridging cyano group) lie in the equatorial plane at normal distances (Table 2, Fig. 1); the axial positions are occupied by one N atom from bpy at a somewhat longer distance of 2.239 (4) Å, and one N atom from the bridging cyano group at a long distance of 2.676 (5) Å. A search in the Cambridge Structural Database (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1991) among the CuN$_6$ hexacoordinated Cu complexes showed that similar distortion exists in the structure of [Cu(bpy)$_3$](ClO$_4$)$_2$ with somewhat shorter second axial Cu—N bonds: 2.226 (7) and 2.450 (7) Å (Anderson, 1972). A value of 2.627 (9) Å for the Cu—N bond was found in the complex [Cu$_3$(bep)$_2$(μ-N$_3$)$_6$] [bep = 2-benzoylpyridine (Goher & Mak, 1985)] and Cu—N bonds with values of 2.593 Å were found in two complexes: [Cu(aep)$_2$(NCS)$_2$] [aep = 2-(2-aminoethyl)pyridine (Kozlowski & Hodgson, 1975)] and [Cu(im)$_6$](NO$_3$)$_2$ [im = imidazole (McFadden, McPhail, Garner & Mabbs, 1975)]. The formation of a deformed coordination polyhedron around the Cu atom is a manifestation of the Jahn–Teller effect. The bond distances and angles in the bpy ligands are normal (Manriquez, Brito, Andrade, Wittke, von Schnering & Peters, 1988).

The distances between Ag atoms are short (Table 2) and account for the metal–metal interaction. The distances are shorter than the 3.222 (1) Å found in the similar complex [Zn(en)$_2$NCAgCN][Ag(CN)$_2$] (Kappenstein, Ouali, Guerin, Černák & Chomič, 1988) and comparable with the value of 3.032 (1) Å found in Ag$_3$(NSO$_2$)$_3$.3H$_2$O (Dalgaard, Hazell & Hazell, 1974). The comparable distance in the metal is 2.89 Å (Wells, 1984). The bond distances and angles in the [Ag(CN)$_2$]$^-$ anions are normal (Zabel, Kühnel & Range, 1989).