formation processes are indicated. The enclathration of chiral aromatic species, *e.g.* *sec*-butylbenzene, by host complexes (2) and (3) is envisaged. We hope that the enantiomeric selectivity of inclusion will be enhanced by having host molecules with different ligands in uneven ratios, thereby reducing the overall symmetry of the host structure. Further work in this area is in progress.

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Potassium Naphthionate*

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Abstract. $C_{10}H_8NO_3S^-.K^+$, $M_r = 261{\cdot}3$, orthorhombic, $P2_1cn$ (non-standard setting of $Pna2_1$), $a = 34{\cdot}478$ (20), $b = 8{\cdot}512$ (8), $c = 7{\cdot}019$ (5) Å, $V = 2059{\cdot}9$ Å^3, $Z = 8$, $D_m = 1{\cdot}681$ (5), $D_x = 1{\cdot}685$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}69$ mm^{-1}, $F(000) = 1072$, room temperature, $R = 0{\cdot}043$ for 1752 reflections $[I > \sigma(I)]$. There are two non-equivalent molecules in each asymmetric unit. Both K^+ ions are seven-coordinated to pentagonal bipyramids of O atoms, with K—O distances of 2·747–2·900 (4) Å. The bond lengths and interbond angles retain standard values; the two non-equivalent naphthalene rings are inclined at 24·46 (5)°.

Introduction. All the naphthionate salts prepared by Corbridge, Brown & Wallwork (1966) resulted in hydrated crystals except those of potassium and thallium. From the crystal structure determinations of the sodium (Brown & Corbridge, 1966) and calcium (Brown, Ehrenberg & Yadav, 1984) salts, it is evident that the crystals retained water of crystallization primarily to complete the coordination sphere around the cation. The structure determination of the potassium salt was undertaken to ascertain how the cation coordination could be satisfied in the anhydrous state, and the suggestion that this would be possible because of the larger size of the K^+ ion is confirmed.

Experimental. Crystals, pink to brown in colour, by slow evaporation of a neutral solution of naphthionic acid in aqueous potassium hydroxide; density by flotation in a CCl_4/dibromobenzene mixture; lattice parameters by least-squares analysis of the separations of 46 $\alpha_1\alpha_2$ doublets (Main & Woolfson, 1963) in a 57·3 mm radius camera and refined on the diffractometer; crystal 0·22 × 0·17 × 0·21 mm mounted about **b** on a Stoe Stadi-2 diffractometer for intensity measurements, supplemented by a small number of visually estimated data from **c** Weissenberg photographs which were used for cross correlation of the layers and also for planes where $\theta < 5°$. 2179 reflections measured, 427 considered unobserved. Index range h 0–44, k 0–11, l 0–8, no correction for absorption or extinction. Three different direct-methods programs gave no solution to the structure which was solved using a special modification (Sheldrick, 1976*a*) of the *SHELX* program (Sheldrick, 1976*b*). Least-squares refinement on F using NRC programs (Ahmed,

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* Potassium 4-amino-1-naphthalenesulfonate. (Note that the atomic numbering used throughout corresponds to the alternative description 1-amino-4-naphthalenesulfonate.)

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Hall, Pippy & Huber, 1970) on a VAX 11/750 computer, introducing anisotropic thermal parameters and H atoms at appropriate stages; H-atom coordinates calculated at idealized positions and included in structure-factor calculations with $B_{\rm iso} = 6{\cdot}0$ Å^2 but not refined; the 427 unobserved reflections all had $F_{\rm calc} < 8{\cdot}0$. During last cycle of refinement $\Delta < 0{\cdot}1\sigma$, max. $\Delta\rho$ excursions in final difference map $\pm 0{\cdot}2$ e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1962); $R = 0{\cdot}043$, $wR = 0{\cdot}075$, $w = 1/F_o^2$.

Table 1. *Final atomic parameters and e.s.d.'s*

$$B_{\rm eq} = \tfrac{4}{3}(\beta_{11}/a^{*2} + \beta_{22}/b^{*2} + \beta_{33}/c^{*2}).$$

	x	y	z	$B_{\rm eq}$(Å^2)
K(1)	0·4784 (–)	0·8354 (2)	0·4904 (2)	2·93 (2)
K(2)	0·5247 (1)	0·1636 (2)	0·7885 (2)	2·46 (2)
S(1)	0·4456 (1)	0·0384 (2)	1·0192 (2)	2·62 (2)
S(2)	0·5582 (1)	0·5316 (2)	0·7616 (2)	2·85 (2)
O(1)	0·4408 (1)	−0·0858 (5)	1·1587 (6)	2·48 (6)
O(2)	0·4602 (1)	−0·0355 (6)	0·8466 (7)	3·55 (8)
O(3)	0·4689 (1)	0·1706 (5)	1·0830 (6)	3·34 (8)
O(4)	0·5659 (1)	0·4211 (5)	0·6089 (6)	2·51 (6)
O(5)	0·5410 (1)	0·4624 (5)	0·9319 (6)	2·37 (6)
O(6)	0·5352 (2)	0·6664 (7)	0·7040 (8)	4·06 (10)
N(1)	0·2902 (2)	0·3230 (7)	0·8985 (8)	3·49 (10)
N(2)	0·7135 (1)	0·8078 (6)	0·8832 (7)	2·45 (7)
C(1)	0·3274 (2)	0·2551 (11)	0·9183 (14)	4·48 (14)
C(2)	0·3584 (2)	0·3483 (8)	0·9692 (10)	3·32 (11)
C(3)	0·3953 (2)	0·2836 (7)	0·9898 (8)	2·59 (9)
C(4)	0·4012 (2)	0·1252 (8)	0·9515 (9)	2·82 (9)
C(5)	0·3699 (2)	0·0310 (8)	0·8992 (9)	3·10 (10)
C(6)	0·3757 (2)	−0·1267 (7)	0·8616 (9)	2·66 (9)
C(7)	0·3451 (2)	−0·2211 (8)	0·8087 (10)	3·05 (10)
C(8)	0·3083 (2)	−0·1576 (7)	0·7914 (9)	3·16 (11)
C(9)	0·3033 (2)	0·0018 (8)	0·8273 (10)	3·21 (11)
C(10)	0·3333 (2)	0·0977 (7)	0·8795 (8)	2·55 (9)
C(11)	0·6765 (2)	0·7437 (8)	0·8608 (10)	2·85 (10)
C(12)	0·6456 (2)	0·8380 (10)	0·8035 (11)	4·03 (14)
C(13)	0·6086 (2)	0·7753 (9)	0·7810 (9)	2·85 (10)
C(14)	0·6036 (2)	0·6166 (8)	0·8196 (9)	2·81 (9)
C(15)	0·6339 (2)	0·5215 (8)	0·8781 (11)	3·42 (11)
C(16)	0·6277 (2)	0·3617 (7)	0·9141 (8)	2·26 (8)
C(17)	0·6580 (2)	0·2653 (9)	0·9726 (11)	3·68 (12)
C(18)	0·6944 (2)	0·3336 (9)	0·9915 (11)	3·75 (13)
C(19)	0·7016 (2)	0·4918 (7)	0·9561 (8)	2·58 (9)
C(20)	0·6709 (2)	0·5848 (8)	0·8976 (10)	3·46 (11)

Table 2. *Bond lengths* (Å)

K(1)—O(6)	2·856 (6)	K(2)—O(2)	2·824 (5)
K(1)—O($2^{\rm iii}$)	2·802 (5)	K(2)—O(3)	2·823 (5)
K(1)—O($1^{\rm i}$)	2·747 (4)	K(2)—O(4)	2·900 (4)
K(1)—O($1^{\rm v}$)	2·754 (4)	K(2)—O(5)	2·792 (4)
K(1)—O($2^{\rm v}$)	2·815 (5)	K(2)—O($4^{\rm ii}$)	2·756 (4)
K(1)—O($5^{\rm iv}$)	2·793 (4)	K(2)—O($3^{\rm v}$)	2·787 (5)
K(1)—O($6^{\rm iv}$)	2·808 (6)	K(2)—O($5^{\rm v}$)	2·781 (4)
S(1)—O(1)	1·450 (5)	S(2)—O(4)	1·450 (4)
S(1)—O(2)	1·455 (5)	S(2)—O(5)	1·458 (4)
S(1)—O(3)	1·454 (5)	S(2)—O(6)	1·451 (6)
S(1)—C(4)	1·767 (7)	S(2)—C(14)	1·770 (7)
N(1)—C(1)	1·414 (10)	N(2)—C(11)	1·397 (8)
C(1)—C(2)	1·377 (11)	C(11)—C(12)	1·392 (11)
C(1)—C(10)	1·382 (12)	C(11)—C(20)	1·390 (10)
C(2)—C(3)	1·396 (9)	C(12)—C(13)	1·393 (11)
C(3)—C(4)	1·389 (9)	C(13)—C(14)	1·388 (11)
C(4)—C(5)	1·393 (9)	C(14)—C(15)	1·386 (10)
C(5)—C(6)	1·384 (9)	C(15)—C(16)	1·400 (9)
C(5)—C(10)	1·390 (8)	C(15)—C(20)	1·389 (10)
C(6)—C(7)	1·379 (9)	C(16)—C(17)	1·392 (10)
C(7)—C(8)	1·383 (10)	C(17)—C(18)	1·389 (11)
C(8)—C(9)	1·391 (9)	C(18)—C(19)	1·391 (10)
C(9)—C(10)	1·369 (9)	C(19)—C(20)	1·384 (9)

Symmetry codes: (i) x, $1+y$, $z-1$; (ii) x, $\tfrac{1}{2}-y$, $z+\tfrac{1}{2}$; (iii) x, $1+y$, z; (iv) x, $1\tfrac{1}{2}-y$, $z-\tfrac{1}{2}$; (v) x, $\tfrac{1}{2}-y$, $z-\tfrac{1}{2}$.

Discussion. The atomic coordinates and equivalent isotropic temperature factors are given in Table 1,* and the bond lengths in Table 2, which also includes the relevant symmetry codes.

The coordination of K$^+$ ions to sulfonate O atoms is sevenfold, the O atoms forming two pentagonal bipyramids with K(1)—O 2·747 (4)–2·856 (6) Å and K(2)—O 2·756 (4)–2·900 (4) Å. The bipyramid around K(1) comprises O(6) and O($1^{\rm i}$) at the apices and O($1^{\rm v}$), O($2^{\rm iii}$), O($2^{\rm v}$), O($6^{\rm iv}$) and O($5^{\rm iv}$) lying in a slightly-distorted plane (mean out-of-plane distance 0·14 Å) around the equator; the sum of the angles subtended at K(1) by these five equatorial O atoms is 355·53°. The corresponding coordination of K(2) comprises O($3^{\rm v}$) and O($4^{\rm ii}$) at the apices and O(2), O(3), O(5), O(4) and O($5^{\rm v}$) in the equatorial plane (mean out-of-plane distance 0·13 Å); the angle sum subtended at K(2) is 357·7°. The two bipyramids share an edge formed by atoms O(2) and O(5).

Potassium is known to show six-, seven-, eight- or ninefold coordination in salts of organic acids. Our mean K—O value of 2·802 Å is in good agreement with the average values in other structures where potassium is seven-coordinated, *e.g.*, K—O in potassium *trans*-aconitate (Carrell, 1973) (which has 3K$^+$ each seven-

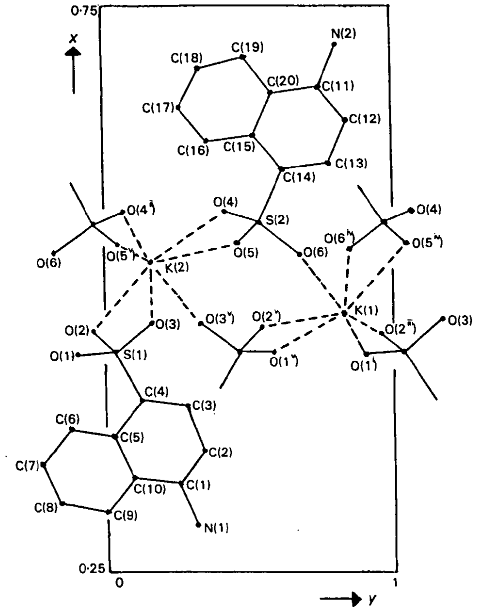

Fig. 1. Projection of part of the unit-cell contents on (001), showing numbering of atoms and coordination of K$^+$ ions (represented by dashed lines). Symmetry codes are defined in Table 2.

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* Lists of structure factors, anisotropic thermal parameters, bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43784 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

coordinated), 2·83 Å; potassium *o*-nitrophenolate hemihydrate (Anderson & Anderson, 1975), 2·83 Å; potassium 5-ethylbarbiturate 5/3-hydrate (Gartland, Gatehouse & Craven, 1975) ($3K^+$ each seven-coordinated), 2·80 Å; and potassium violurate dihydrate (Gillier, 1965), 2·80 Å.

In the naphthalene rings there is no apparent alternation in length of the C—C bonds as was observed in the sodium (Brown & Corbridge, 1966) and calcium (Brown *et al.*, 1984) salts. The naphthalene rings are essentially regular and planar, the mean out-of-plane distances being 0·006 Å for the C(1)–(10) atoms and 0·002 Å for the C(11)–(20) atoms. The dihedral angle between the mean planes through the naphthalene rings is 24·46 (5)°.

The peculiar reversible flexibility shown by the crystals, *i.e.* they can readily be bent between the fingers if large enough, can be explained by referring to a model of the structure. The molecules lie in layers approximately parallel to (001) and there are no strong bonding forces across (100): hence *c* is the flex axis and (100) readily curves on bending.

Fig. 1 shows the atomic numbering used and the arrangement of the molecules in (001) projection.

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Bis(methyltriphenylphosphonium) Di-μ-bromo-dibromodicuprate(I)

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Abstract. $[P(CH_3)(C_6H_5)_3]_2[Cu_2Br_4]$, $M_r = 1001·4$, monoclinic, $C2/c$, $a = 22·937$ (9), $b = 9·288$ (4), $c = 19·280$ (12) Å, $\beta = 106·71$ (4)°, $V = 3934$ (3) Å^3, $Z = 4$, $D_x = 1·69$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 55·3$ cm^{-1}, $F(000) = 1968$, $T = 290$ K, $R = 0·047$ for 2580 unique observed reflections $[I \geq 3\sigma(I)]$ and 262 parameters. The $[Cu_2Br_4]^{2-}$ anion is a centrosymmetric dimer containing approximately trigonal-planar coordinated Cu^I. The Cu—Br(terminal) distance is 2·337 (2) Å, the Cu—Br(bridging) distances are 2·426 (2) and 2·455 (1) Å and the Cu···Cu separation 2·697 (2) Å.

Introduction. In halocuprates(I) crystallizing with symmetrically substituted tetraalkylammonium and related unipositive cations there would appear to be a correlation between the coordination number of Cu^I and the concentration of halide ligand in the crystalline phase, suggesting that the degree of dilution imposed on the ligands by the cations determines the Cu^I coordination in the resulting anion (Andersson & Jagner, 1986*a*). In order to examine the effect of cation size further, as well as lack of symmetry with respect to exposure of the positive charge, attempts are being made to prepare crystalline halocuprates(I) containing unsymmetrically substituted quaternary alkylammonium and related unipositive cations. Butyltriphenylphosphonium has been found to crystallize with a linear $[CuBr_2]^-$ monomer and with a $[Cu_4Br_6]^{2-}$ aggregate containing three-coordinated Cu^I (Andersson & Jagner, 1986*b*), whereas propyltriphenylphosphonium (Andersson & Jagner, 1985*c*) and ethyltriphenylphosphonium (Andersson & Jagner, 1985*b*) both crystallize with digonal, monomeric dibromocuprate(I) anions.

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