

C14	-0.1041 (8)	0.1702 (6)	0.4443 (6)	0.0301 (13)
C15	0.0502 (8)	0.1818 (6)	0.3313 (7)	0.0299 (13)
N2	0.3264 (6)	0.3269 (5)	0.1408 (5)	0.0259 (10)
C21	0.2972 (9)	0.4508 (6)	0.1926 (7)	0.0351 (14)
C23	0.2309 (9)	0.5593 (7)	-0.0040 (7)	0.044 (2)
C24	0.2604 (10)	0.4317 (8)	-0.0536 (7)	0.045 (2)
C22	0.2480 (10)	0.5683 (7)	0.1208 (8)	0.043 (2)
C25	0.3089 (9)	0.3160 (7)	0.0198 (6)	0.0351 (14)
O	0.4692 (8)	0.1066 (7)	0.6944 (7)	0.0597 (15)
H1	0.378 (11)	0.083 (9)	0.754 (8)	0.07 (3)
H2	0.473 (19)	0.188 (9)	0.675 (13)	0.14 (5)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Os1—F11	1.924 (3)	C12—C13	1.364 (9)
Os1—F12 <sup>i</sup>	1.938 (3)	C13—C14	1.383 (8)
Os1—C11	2.341 (2)	C14—C15	1.363 (8)
Os2—F21	1.938 (3)	N2—C25	1.344 (8)
Os2—F22	1.944 (3)	N2—C21	1.353 (7)
Os2—C12	2.334 (2)	C21—C22	1.368 (9)
CM—N1	1.469 (7)	C23—C22	1.376 (10)
CM—N2	1.475 (8)	C23—C24	1.378 (10)
N1—C11	1.340 (8)	C24—C25	1.363 (10)
N1—C15	1.367 (8)	F12...O	2.897 (7)
C11—C12	1.363 (9)	F22...O	2.845 (7)
F11—Os1—F12 <sup>i</sup>	89.9 (2)	F21—Os2—C12 <sup>iv</sup>	90.67 (11)
F11—Os1—F12 <sup>ii</sup>	90.1 (2)	F21—Os2—C12	89.33 (11)
F11—Os1—C11 <sup>iii</sup>	91.41 (11)	F22—Os2—C12 <sup>iv</sup>	91.32 (12)
F11—Os1—C11	88.58 (11)	F22—Os2—C12	88.68 (12)
F12 <sup>i</sup> —Os1—C11	91.00 (11)	N1—CM—N2	109.3 (5)
F12 <sup>ii</sup> —Os1—C11	89.00 (11)	F22...O...F12	103.5 (2)
F21—Os2—F22 <sup>iv</sup>	89.0 (2)	H1—O—H2	122 (10)
F21—Os2—F22	91.0 (2)		

Symmetry codes: (i)  $x, y, z - 1$ ; (ii)  $-x, -y, 1 - z$ ; (iii)  $-x, -y, -z$ ; (iv)  $1 - x, 1 - y, 1 - z$ .

Data collection: *CAD-4-PC* (Enraf-Nonius, 1993). Cell refinement: *CAD-4-PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1020). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Three Polymorphs of Potassium 4-Sulfonatobenzoic Acid

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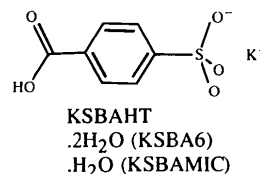
(Received 11 April 1994; accepted 2 November 1994)

## Abstract

The structures of the dihydrate, monohydrate and anhydrous forms of  $\text{K}^+\cdot\text{CO}_2\text{H}(\text{C}_6\text{H}_4)\text{SO}_3^-$  have been solved. Each  $\text{K}^+$  cation interacts with nine O atoms in the dihydrate and with seven in the other two structures. Electrostatic forces and hydrogen bonds hold the layered structures together.

## Comment

Many instances of polymorphism in organic salts have become evident during a study of solid-state reactivity. For example, five crystalline forms of magnesium hydrogen phthalate have been observed (Kariuki & Jones, 1989, 1992). While investigating salts of derivatives of benzoic acid, three polymorphs of potassium 4-sulfonatobenzoic acid have been obtained,  $\text{K}^+\cdot\text{C}_7\text{H}_5\text{O}_5\text{S}^- \cdot 2\text{H}_2\text{O}$  (KSBA6),  $\text{K}^+\cdot\text{C}_7\text{H}_5\text{O}_5\text{S}^- \cdot \text{H}_2\text{O}$  (KSBAMIC) and  $\text{K}^+\cdot\text{C}_7\text{H}_5\text{O}_5\text{S}^-$  (KSBAHT).



In the anions, the interplanar angles between the phenyl rings and carboxylate ( $\text{CO}_2$ ) groups are  $1.87(28)^\circ$  for KSBA6,  $1.18(7)^\circ$  for KSBAMIC and

4.06 (28)° for KSBAHT; the r.m.s. deviations of the carboxylic protons from the CO<sub>2</sub> planes are 0.097 (33), 0.015 (25) and 0.090 (24) Å, respectively. The benzoic acid segment of each anion is, therefore, essentially planar. The SO<sub>3</sub> groups are deprotonated while the carboxylic groups are not, similar to 2-sulfonatobenzoic acid salts (Okaya, 1967; Teplova, Turskaya, Shibanovo, Nekrasov & Belikova, 1986; Teplova *et al.*, 1984; Attig

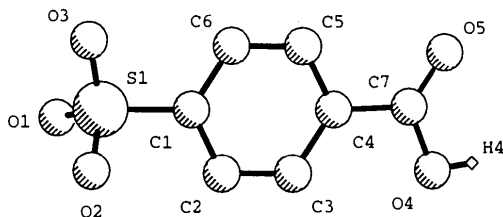


Fig. 1. The anion atom-numbering scheme used for the three structures.

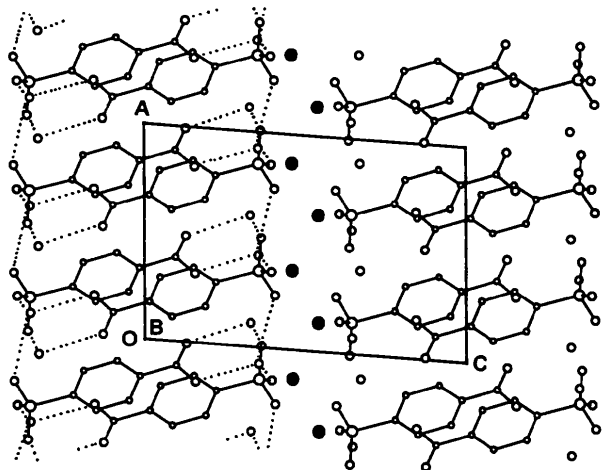


Fig. 2. The structure of KSBA6 viewed down the *b* axis. Filled circles represent K<sup>+</sup> ions, H atoms have been omitted for clarity and dotted lines represent hydrogen bonds.

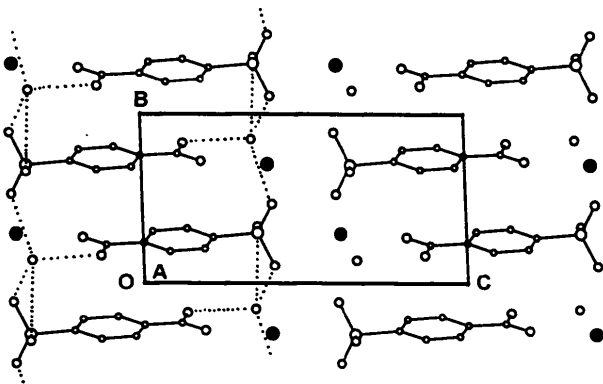


Fig. 3. The structure of KSBAMIC viewed down the *a* axis. Filled circles represent K<sup>+</sup> ions, H atoms have been omitted for clarity and dotted lines represent hydrogen bonds.

& Mootz, 1976). In each anion, the S—O bond distances are equivalent and the O—S—O angles are larger than the C—S—O angles.

KSBA6 contains two independent water molecules while KSBAMIC contains one. In these two crystal structures, hydrogen bonding occurs between the anion and water molecules. There is no direct bonding between anions, unlike in KSBAHT. The three crystal structures are composed of ionic layers which are separated by aromatic rings and carboxylic groups.

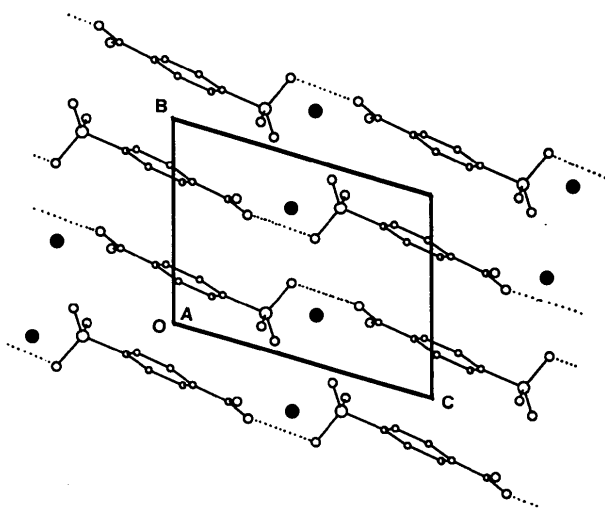


Fig. 4. The structure of KSBAHT viewed down the *a* axis. Filled circles represent K<sup>+</sup> ions, H atoms have been omitted for clarity and dotted lines represent hydrogen bonds.

## Experimental

KSBA6 was obtained by recrystallization from a solution of potassium 4-sulfonatobenzoic acid in water at 295 K. Maintaining the temperature of the solution above 323 K yielded KSBAHT. A solution of the salt in a mixture of water and ethanol (3:1 volume ratio) gave KSBAMIC. The crystals were obtained together with a microcrystalline mixture of other phases when all the solvent was allowed to evaporate off at 295 K. The crystal of KSBA6 used for data collection was sealed in a capillary tube to reduce deterioration in the X-ray beam.

### KSBA6

#### Crystal data

$K^+.C_7H_5O_5S^-.2H_2O$

$M_r = 276.30$

Monoclinic

$P2_1/a$

$a = 8.6449 (10) \text{ \AA}$

$b = 9.9416 (10) \text{ \AA}$

$c = 12.892 (2) \text{ \AA}$

$\beta = 94.96 (9)^\circ$

$V = 1103.9 (2) \text{ \AA}^3$

$Z = 4$

$D_x = 1.663 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 7-15^\circ$

$\mu = 0.687 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Transparent block

$0.3 \times 0.2 \times 0.2 \text{ mm}$

Colourless

**Data collection**

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.0176$
$2\theta/\omega$ scans	$\theta_{\text{max}} = 24.97^\circ$
Absorption correction: none	$h = -10 \rightarrow 10$
2037 measured reflections	$k = 0 \rightarrow 11$
1948 independent reflections	$l = 0 \rightarrow 15$
1402 observed reflections [ $I > 2\sigma(I)$ ]	3 standard reflections monitored every 100 reflections
	intensity decay: none

**Refinement**

Refinement on $F^2$	$\Delta\rho_{\text{max}} = 0.309 \text{ e } \text{Å}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.0335$	$\Delta\rho_{\text{min}} = -0.305 \text{ e } \text{Å}^{-3}$
$wR(F^2) = 0.0812$	Extinction correction: <i>SHELXL93</i> (Sheldrick, 1993)
$S = 1.221$	Extinction coefficient: 0.046 (3)
1947 reflections	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
170 parameters	
H atoms refined as riding or free	
$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\text{max}} = -0.012$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2$ ) for KSBA6

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
K1	0.13349 (6)	0.26670 (6)	0.54021 (4)	0.0403 (2)
S1	0.14656 (7)	0.60865 (6)	0.64445 (4)	0.0318 (2)
O1	0.1471 (2)	0.7455 (2)	0.60521 (13)	0.0420 (5)
O2	-0.0079 (2)	0.5524 (2)	0.63742 (14)	0.0512 (5)
O3	0.2565 (2)	0.5258 (2)	0.59485 (14)	0.0502 (5)
O4	0.3195 (3)	0.5378 (2)	1.1560 (2)	0.0593 (6)
O5	0.4920 (3)	0.6968 (2)	1.12885 (15)	0.0605 (6)
O6	0.6109 (2)	0.7850 (2)	1.3287 (2)	0.0480 (5)
O7	0.0752 (3)	0.0175 (2)	0.64543 (15)	0.0441 (5)
C1	0.2138 (3)	0.6143 (2)	0.7785 (2)	0.0307 (5)
C2	0.1539 (3)	0.5269 (3)	0.8480 (2)	0.0446 (7)
C3	0.2103 (3)	0.5287 (3)	0.9508 (2)	0.0464 (7)
C4	0.3276 (3)	0.6161 (2)	0.9852 (2)	0.0346 (6)
C5	0.3880 (3)	0.7020 (3)	0.9149 (2)	0.0438 (7)
C6	0.3309 (3)	0.7031 (3)	0.8114 (2)	0.0421 (6)
C7	0.3886 (3)	0.6217 (3)	1.0969 (2)	0.0407 (6)

Table 2. Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ ) for KSBA6

K1—O6 <sup>i</sup>	2.713 (3)	S1—C1	1.776 (2)
K1—O1 <sup>ii</sup>	2.788 (3)	O4—C7	1.308 (3)
K1—O6 <sup>iii</sup>	2.824 (3)	O5—C7	1.210 (3)
K1—O3	2.852 (2)	C4—C7	1.492 (3)
K1—O7	2.890 (2)	C—C(ring-mean)	1.379 (4)
K1—O1 <sup>iv</sup>	2.937 (3)	O1—O7 <sup>*</sup>	2.832 (3)
K1—O2 <sup>iv</sup>	3.038 (2)	O3—O7 <sup>vi</sup>	2.809 (3)
K1—O3 <sup>ii</sup>	3.155 (2)	O4—O7 <sup>vii</sup>	2.650 (3)
K1—O2	3.376 (2)	O5—O6	2.829 (3)
S1—O(mean)	1.447 (2)	O6—O2 <sup>vii</sup>	2.849 (3)
O—S1—O(mean)	111.93 (12)	C5—C4—C7	119.3 (2)
O—S1—C(mean)	106.89 (11)	C—C—C(ring-mean)	120.0 (2)
C2—C1—S1	120.1 (2)	O5—C7—O4	123.9 (2)
C6—C1—S1	119.2 (2)	O5—C7—C4	122.7 (3)
C3—C4—C7	121.5 (2)	O4—C7—C4	113.4 (2)

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

**KSBAMIC****Crystal data**

$\text{K}^+ \cdot \text{C}_7\text{H}_5\text{O}_5\text{S}^- \cdot \text{H}_2\text{O}$
$M_r = 258.29$
Triclinic
$P\bar{1}$
$a = 6.0576 (10) \text{ Å}$
$b = 6.7412 (10) \text{ Å}$
$c = 12.479 (2) \text{ Å}$
$\alpha = 90.278 (10)^\circ$
$\beta = 95.841 (10)^\circ$
$\gamma = 106.379 (10)^\circ$
$V = 486.05 (13) \text{ Å}^3$
$Z = 2$
$D_x = 1.765 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71069 \text{ Å}$
Cell parameters from 25 reflections
$\theta = 10\text{--}14^\circ$
$\mu = 0.766 \text{ mm}^{-1}$
$T = 293 (2) \text{ K}$
Transparent plate
$0.5 \times 0.4 \times 0.1 \text{ mm}$
Colourless

**Data collection**

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.0106$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 26.96^\circ$
Absorption correction: none	$h = -7 \rightarrow 7$
2215 measured reflections	$k = -8 \rightarrow 8$
2116 independent reflections	$l = 0 \rightarrow 15$
1916 observed reflections [ $I > 2\sigma(I)$ ]	3 standard reflections monitored every 100 reflections
	intensity decay: none

**Refinement**

Refinement on $F^2$	$\Delta\rho_{\text{max}} = 0.534 \text{ e } \text{Å}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.0304$	$\Delta\rho_{\text{min}} = -0.445 \text{ e } \text{Å}^{-3}$
$wR(F^2) = 0.0850$	Extinction correction: <i>SHELXL93</i> (Sheldrick, 1993)
$S = 1.140$	Extinction coefficient: 0.081 (7)
2115 reflections	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
153 parameters	
H atoms refined as riding or free	
$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.1404P]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\text{max}} = -0.018$	

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2$ ) for KSBAMIC

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
K1	0.10980 (6)	0.29474 (6)	0.61015 (3)	0.03282 (14)
S1	0.27666 (6)	0.30230 (6)	0.35438 (3)	0.02730 (14)
O1	0.2125 (2)	0.4735 (2)	0.40114 (10)	0.0409 (3)
O2	0.1708 (3)	0.1100 (2)	0.40344 (11)	0.0496 (4)
O3	0.5238 (2)	0.3419 (3)	0.35466 (11)	0.0524 (4)
O4	-0.3391 (2)	0.1670 (2)	-0.13054 (11)	0.0408 (3)
O5	0.0142 (3)	0.2751 (2)	-0.18459 (10)	0.0437 (3)
O6	0.4998 (2)	-0.1444 (3)	0.34149 (11)	0.0426 (3)
C1	0.1607 (3)	0.2775 (2)	0.21688 (12)	0.0252 (3)
C2	-0.0774 (3)	0.2092 (3)	0.19036 (13)	0.0311 (3)
C3	-0.1673 (3)	0.1921 (3)	0.08326 (13)	0.0303 (3)
C4	-0.0193 (3)	0.2438 (2)	0.00287 (12)	0.0258 (3)
C5	0.2183 (3)	0.3108 (3)	0.03035 (13)	0.0310 (3)
C6	0.3093 (3)	0.3285 (3)	0.13731 (13)	0.0297 (3)
C7	-0.1094 (3)	0.2309 (2)	-0.11347 (13)	0.0304 (3)

Table 4. Selected geometric parameters (Å, °) for KSBAMIC

K1—O5 <sup>i</sup>	2.6788 (14)	O4—C7	1.330 (2)
K1—O2 <sup>ii</sup>	2.7717 (15)	O5—C7	1.204 (2)
K1—O3 <sup>iii</sup>	2.801 (2)	C4—C7	1.491 (2)
K1—O1 <sup>iv</sup>	2.8174 (14)	C—C(ring-mean)	1.387 (2)
K1—O6 <sup>v</sup>	2.8376 (15)	O1—O6 <sup>vi</sup>	2.823 (2)
K1—O1	2.9292 (14)	O2—O6	3.120 (2)
K1—O2	2.960 (2)	O3—O6	3.243 (2)
S1—O(mean)	1.4478 (13)	O4—O6 <sup>vii</sup>	2.700 (2)
S1—C1	1.775 (2)		
O—S1—O(mean)	112.27 (9)	C3—C4—C7	121.67 (14)
O—S1—C(mean)	106.51 (8)	C—C—C(ring-mean)	120.00 (16)
C6—C1—S1	119.49 (12)	O5—C7—O4	123.5 (2)
C2—C1—S1	119.64 (12)	O5—C7—C4	123.1 (2)
C5—C4—C7	118.36 (14)	O4—C7—C4	113.33 (14)

Symmetry codes: (i)  $x, y, 1+z$ ; (ii)  $-x, -y, 1-z$ ; (iii)  $1-x, 1-y, 1-z$ ; (iv)  $-x, 1-y, 1-z$ ; (v)  $1-x, -y, 1-z$ ; (vi)  $x, 1+y, z$ ; (vii)  $-x, -y, -z$ .

## KBSAHT

## Crystal data

K<sup>+</sup>.C<sub>7</sub>H<sub>5</sub>O<sub>5</sub>S<sup>-</sup> $M_r = 240.27$ 

Triclinic

 $P\bar{1}$  $a = 6.3113 (10) \text{ \AA}$  $b = 7.5404 (10) \text{ \AA}$  $c = 9.8868 (10) \text{ \AA}$  $\alpha = 103.832 (10)^\circ$  $\beta = 99.202 (10)^\circ$  $\gamma = 100.707 (10)^\circ$  $V = 438.49 (10) \text{ \AA}^3$  $Z = 2$  $D_x = 1.820 \text{ Mg m}^{-3}$ Mo  $K\alpha$  radiation $\lambda = 0.71069 \text{ \AA}$ 

Cell parameters from 25

reflections

 $\theta = 9-13^\circ$  $\mu = 0.834 \text{ mm}^{-1}$  $T = 293 (2) \text{ K}$ 

Transparent prism

 $0.3 \times 0.1 \times 0.1 \text{ mm}$ 

Colourless

 $R_{\text{int}} = 0.0118$  $\theta_{\text{max}} = 29.96^\circ$  $h = -8 \rightarrow 8$  $k = -10 \rightarrow 10$  $l = 0 \rightarrow 13$ 

3 standard reflections

monitored every 100

reflections

intensity decay: none

## Data collection

Enraf-Nonius CAD-4

diffractometer

2 $\theta/\omega$  scans

Absorption correction:

none

2691 measured reflections

2554 independent reflections

2040 observed reflections

 $[I > 2\sigma(I)]$ 

## Refinement

Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.0299$  $wR(F^2) = 0.0821$  $S = 1.165$ 

2554 reflections

136 parameters

 $w = 1/[\sigma^2(F_o^2) + (0.0470P)^2$  $+ 0.0657P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\text{max}} = 0.001$  $\Delta\rho_{\text{max}} = 0.466 \text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.397 \text{ e \AA}^{-3}$ 

Extinction correction:

 $SHELXL93$  (Sheldrick, 1993)

Extinction coefficient:

0.002 (3)

Atomic scattering factors

from *International Tables*for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for KBSAHT
$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
K1	-0.20683 (6)	0.74425 (5)	0.45351 (4)	0.03168 (11)
S1	0.35166 (6)	0.80987 (5)	0.64833 (4)	0.02373 (11)
O1	0.5857 (2)	0.8786 (2)	0.66607 (14)	0.0437 (3)
O2	0.2203 (2)	0.9371 (2)	0.61401 (14)	0.0402 (3)
O3	0.2704 (3)	0.6236 (2)	0.54658 (13)	0.0459 (4)
O4	0.3346 (2)	0.6411 (2)	1.28506 (13)	0.0357 (3)
O5	0.0068 (2)	0.7113 (2)	1.24144 (14)	0.0454 (3)
C1	0.3047 (2)	0.7808 (2)	0.81470 (15)	0.0231 (3)
C2	0.1094 (3)	0.8050 (3)	0.8550 (2)	0.0360 (4)
C3	0.0747 (3)	0.7776 (3)	0.9843 (2)	0.0365 (4)
C4	0.2330 (3)	0.7278 (2)	1.0729 (2)	0.0253 (3)
C5	0.4299 (3)	0.7093 (3)	1.0337 (2)	0.0325 (4)
C6	0.4650 (3)	0.7344 (3)	0.9033 (2)	0.0325 (4)
C7	0.1793 (3)	0.6953 (2)	1.2078 (2)	0.0289 (3)

Table 6. Selected geometric parameters (Å, °) for KBSAHT

K1—O2 <sup>i</sup>	2.6555 (13)	S1—O(mean)	1.4482 (13)
K1—O5 <sup>ii</sup>	2.6562 (13)	S1—C1	1.7735 (14)
K1—O3 <sup>iii</sup>	2.7277 (13)	O4—C7	1.331 (2)
K1—O1 <sup>iv</sup>	2.7410 (14)	C4—C7	1.492 (2)
K1—O2	2.824 (2)	C—C(ring-mean)	1.386 (2)
K1—O4 <sup>v</sup>	2.9591 (15)	O3—O4 <sup>ii</sup>	2.710 (2)
K1—O3	3.358 (2)		
O—S1—O(mean)	112.51 (9)	C3—C4—C7	117.27 (14)
O—S1—C(mean)	106.22 (7)	C—C—C(ring-mean)	119.99 (18)
C6—C1—S1	119.27 (11)	O5—C7—O4	123.08 (15)
C2—C1—S1	120.14 (12)	O5—C7—C4	122.7 (2)
C5—C4—C7	122.97 (14)	O4—C7—C4	114.17 (14)

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

For all the structures, all non-H atoms were assigned anisotropic displacement parameters. The positions of the ring H atoms were fixed geometrically and the difference Fourier synthesis map revealed the positions of the carboxylic and water protons.

For all compounds, data collection: Enraf-Nonius CAD-4 software; cell refinement: Enraf-Nonius CAD-4 software; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *DTMM* (Crabbe & Appleyard, 1991); software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## An Unexpected By-Product in the Friedel–Crafts Acrylation of Ferrocene

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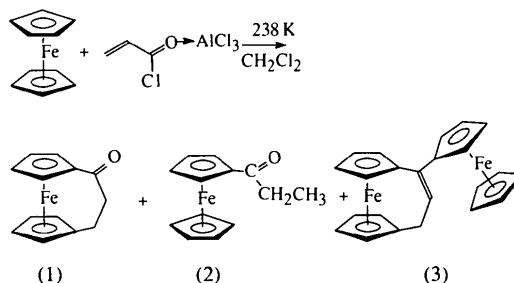
### Abstract

The structure of an unsaturated [3]ferrocenophane derivative, 1,1'-(1-ferrocenyl-1,3-propenediyl)ferrocene,  $[\text{Fe}_2(\text{C}_5\text{H}_5)(\text{C}_{18}\text{H}_{15})]$ , has been determined. Because of the double bond, the three-carbon bridge and the directly attached C atoms are essentially coplanar. Strain in the bridged structure is manifested in a ring-tilt angle of  $12.3^\circ$  and in opening of the angles in the bridge.

### Comment

The Friedel–Crafts reaction of ferrocene with acrylyl chloride and aluminium chloride constitutes a very convenient one-pot synthetic route to the bridged [3]ferrocenophane system (Turbit & Watts, 1972). We obtained results somewhat inconsistent with the published procedure in which a dichloromethane solution of acrylyl chloride was added to a solution containing aluminium chloride and ferrocene, but were able to obtain higher and more consistent yields of the desired [3]ferrocenophane-1-one (1) by initial formation of an acid–base complex of acrylyl chloride and aluminium chloride, followed by addition of the complex in dichloromethane solution to a solution of ferrocene at 238 K. Under these conditions, 30–60% yields of the ferrocenophanone were obtained, along with about 10% of propanoylferrocene (2) and a less polar by-product (3). The latter material, (3), melted with decomposition at 423 K. Mass spectral data suggested the composition to be  $\text{Fc}_2\text{C}_3\text{H}_2$  ( $\text{Fc} = \text{C}_5\text{H}_5\text{FeC}_5\text{H}_4$ ), but good NMR spectra were not obtainable because of insufficient solubility. The product formed clusters of red crystals upon

recrystallization from a hexane–dichloromethane mixture and these crystals were used for the structure analysis.



The crystal structure reveals the by-product to be an unsaturated [3]ferrocenophane derivative, 1-(ferrocenyl)- $\Delta^1$ -[3]ferrocenophene. Formation of this product from the [3]ferrocenophanone by acid coordination to the keto group, attack of the cation on an unsubstituted ferrocene and dehydration of the resulting tertiary alcohol is readily envisaged.

Because of the double bond in the three-carbon bridge, atoms C1, C23, C11, C22 and C21 form a plane approximately orthogonal to the planes of the two cyclopentadienyl rings of the bridged ferrocene. The tilt angle between the two rings of the bridged ferrocene unit is  $12.3^\circ$ ; this value falls within the normal range of about  $7$ – $14^\circ$  found in other [3]ferrocenophanes, e.g.  $7.4^\circ$  in 1,1'-trimethyleneferrocene (Hillman & Austin, 1987),  $8.8^\circ$  in [3]ferrocenophan-1-one (Jones, Marsh & Richards, 1965),  $10^\circ$  in 1,1'-( $\alpha$ -keto- $\gamma$ -phenyltrimethylene)-2'-methylferrocene (Lecomte, Dusausoy, Protas & Moïse, 1973),  $10^\circ$  in 3,3'-trimethylene[1.1]ferrocenophane (Singletary, Hillman, Dauplaise, Kwick & Kerber, 1984),  $12^\circ$  in 2,2'-trimethylene[1.1]ferrocenophane (Singletary *et al.*, 1984),  $12.9$  and  $13.6^\circ$  in 1,1'-(propane-1,3-diyl)ferrocenium iodide (Dong *et al.*, 1991) and  $13.6^\circ$  in 2-benzylidene[3]ferrocenophane-1,3-dione (Gyepes, Glowiak & Toma, 1986). In addition, both ferrocene units are eclipsed, and the disorder

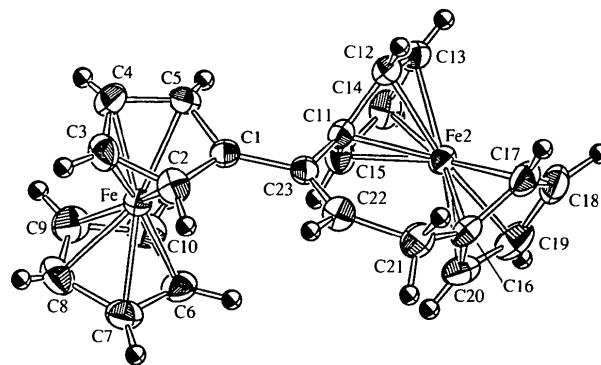


Fig. 1. ORTEP (Johnson, 1976) drawing of 1-(ferrocenyl)- $\Delta^1$ -[3]ferrocenophene with 50% probability displacement ellipsoids.