Short Communication

The Structure of Potassium Sulfite

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In a series of *ab initio* calculations on sulfite and
hydrogensulfite ions, SO_3^{2-}, HSO_3^- and
SO_2OH^-,[1] the calculated S–O bond distance in
SO_3^{2-} was 0.05 Å longer than that found in
Na_2SO_3;[2] however, the Na_2SO_3 structure was de-
termined from a twinned crystal. Therefore, the
structure of K_2SO_3 was investigated in order to
get a better experimental model which could be
useful for a comparison with accurate theoretical
studies. In our theoretical calculations, we as-
sumed that the interaction between the SO_3^{2-}
ions and the surrounding ions is purely electro-
static, the surrounding ions being represented by
point charges using the Ewald technique.[3] There-
fore, in making comparisons between theoretical
and experimental data, we needed a crystal struc-
ture where this assumption was valid. Further-
more, it was possible to cut down the computing
time for the theoretical calculations substantially
if the crystal structure had high symmetry. Both
of these prerequisites where fullfilled in the struc-
tures of K_2SO_3 and $Tl_3Na(SO_3)_2$.[4] K_2SO_3 was cho-
sen in order to have the series K_2SO_3, K_2SeO_3,[5,6]
and K_2TeO_3[7] structures for comparison purposes.
The crystals were prepared in a sealed pyrex glass
ampoule. After 6 days at 200 °C, irregular prisms
of approximate dimensions 0.2×0.2×0.2 mm
formed. To avoid oxidation, they were covered
with epoxy glue.

Relevant crystallographic data are given in
Table 1. Atomic distances and angles are given in
Table 2; atomic coordinates and equivalent iso-
tropic temperature factors in Table 3.

The sulfite group is situated on a three-fold
axis (see Fig. 1) as in the case of Na_2SO_3 and

$Tl_3Na(SO)_2$ but the mirror plane is not present in
Na_2SO_3 (space group P_3^-). However, the S–O
distance showed no significant difference, within
3 sigmas: 1.515(1), 1.504(3), 1.51(3) in K_2SO_3,
Na_2SO_3 and $Tl_3Na(SO_3)_2$, respectively.

Table 1. Summary of crystal data, intensity collection
and structure refinement of K_2SO_3.

(a) Crystal data	
Formula	K_2SO_3
Mol.wt.	158.2
Crystal system	Hexagonal
Space group	P3m1
a, Å	5.915(1)
c, Å	6.968(2)
V, Å³	211(1)
Z	2
d_{calc}, g.cm⁻³	2.49
Radiation	MoKα (λ = 0.71069 Å)
μ(MoKα), cm⁻¹	25.2

(b) Data collection and structure refinement[a]	
2θscanspeed, deg min⁻¹	2.0–29.3° (θ/2θ)
No. of data collected	714 (2θ ≤ 70°)
No. of unique data ($I_{obs} > 3\sigma(I_{obs})$)	490
Abs. correction	empirical (max. reduction in intensity 37%)
Structure solution	Patterson
R, %	2.8
R_w, % ($w = 1/\sigma^2$)	3.3

[a]Programs used: LELA,[9,10] XTL,[11] LINUS[12,13].
Scattering factors taken from Ref. 14.
List of $F_o - F_c$ values and anisotropic temperature
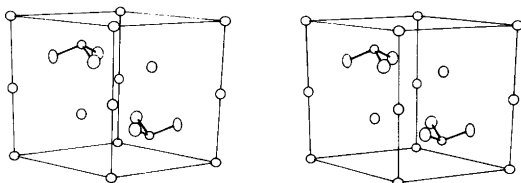factors are available from the author on request.

Table 2. Selected distances (Å) and angles (°) in K₂SO₃.

K1–O$^{(i-v)}$ (6x)	2.764(1)
K2–O$^{(ii,iv,vi-vii)}$ (6x)	2.583(1)
K3–O$^{(vi,xi-xv)}$ (6x)	3.000(1)
–O$^{(ix,x)}$ (3x)	3.143(2)
O–K1–O$^{(iii)}$	180.0
–K1–O$^{(ii)}$	78.75(5)
–K2–O$^{(iii)}$	180.0
–K2–O$^{(ii)}$	85.60(6)
S–O$^{(ix,x)}$(3x)	1.515(1)
O–S–O$^{(x)}$	105.2(1)

Symmetry codes: (*i*) $y,x,-z$ (*ii*) $-y,-x,z$
(*iii*) $-x,-y,-z$ (*iv*) $y-x,-x,z$ (*v*) $-x,y-x,-z$
(*vi*) $y,x,1-z$ (*vii*) $-x,-y,1-z$ (*viii*) $-x,y-x,1-z$
(*ix*)1 $-x,1-y,z$ (*x*) $y-x,1-x,z$ (*xi*) $1-x, 1-y, 1-z$
(*xii*) $y,1+x,1-z$ (*xiii*) $-x,1-y,1-z$ (*xiv*)
$1-x,1-+y-x,1-z$
(*xv*) $-x,y-x,1-z$

Table 3. Fractional coordinates and equivalent isotropic temperature factors[15] for K₂SO₃.

Atom	x	y	z	B
K1	0.0	0.0	0.0	1.79(1)
K2	0.0	0.0	0.5	1.90(1)
K3	1/3	2/3	0.6746(1)	1.96(1)
S	1/3	2/3	0.1835(1)	1.40(1)
O	0.1977(2)	0.3954(2)	0.2700(2)	2.75(5)

The structure of K₂SO₃ has been used as a model in *ab initio* MO calculations on the sulfite system.[8] A S–O bond of 1.526 Å was obtained in these calculations with the inclusion of the crystal field of K₂SO₃. This value is in closer agreement with experiment than the previous one (1.554 Å) calculated with Na₂SO₃ as a model. There are different types of K–O coordination: two six-fold and one nine-fold. The coordination distance for K2 (2.583(1) Å) is short but it is difficult to compare it with values found in other structures because the coordination number is often uncertain and there are no three- or six-fold axes through the potassium atom. As seen from the angles in Table 2, K2 possesses a more perfect octahedron than K1, which supports the notion that the K2 octahedron is a good model for a regular six-fold oxygen coordination around the potassium atom.

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Fig. 1. A stereoscopic view of the K₂SO₃ cell.