

(Camerman *et al.*, 1978). The Co atom deviates only 0.02 and 0.04 Å from the planes of the two imidazole rings (Table 3).*

The geometry of the coordinated nitro group is similar to that found in related complexes (Watson, Johnson, Čelap & Kamberi, 1972; Herak & Prelesnik, 1976; Herak, Prelesnik, Manojlović-Muir & Muir, 1974; Vasić, Herak & Djurić, 1976).

Extensive hydrogen bonding exists in the crystal. All the O atoms are engaged in intra- and intermolecular hydrogen bonds of the type O—H...O and N—H...O (Fig. 1). The most significant interaction exists between the N(3) atom from the imidazole ring of the tridentate histidine ligand and the O(2') atom of the uncoordinated carboxylate group of the bidentate histidine in another adjacent complex molecule. Short N(imidazole)—O(carboxyl) distances are apparent in the structures of orthorhombic and monoclinic L-histidine (Madden, McGandy & Seeman, 1972; Madden, McGandy, Seeman, Harding & Hoy, 1972) and L-N-acetylhistidine (Kistenmacher, Hunt & Marsh, 1972). The N(3)—H(7)...O(2') hydrogen bond of 2.59 Å is, to the best of our knowledge, one of the shortest hydrogen bonds of this type.

* See deposition footnote.

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Structure of Sodium Methanesulfonate*

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Abstract

Sodium methanesulfonate, NaCH₃SO₃, crystallizes in the orthorhombic system, space group *Pbma*, with *a* =

17.0713 (6), *b* = 22.0217 (6), *c* = 5.6058 (3) Å, *Z* = 20, *V* = 2107.4 Å³, *D_c* = 1.861, *D_o* = 1.88 Mg m⁻³ (floatation in bromobenzene/CHBr₃), *M_r* = 118.09, *F*(000) = 5200, μ(Cu Kα) = 6.55 mm⁻¹, transmission = 0.294–0.822 at 297 K. The structure was solved by the heavy-atom technique and refined by the full-matrix least-squares method to *R*(*F*) = 0.027 based on 1953

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nonzero counter data to 0.83 Å. Analytical absorption and anisotropic extinction corrections were applied. The asymmetric unit contains 2.5 molecules, with one CH_3SO_3^- anion on the crystallographic mirror plane in the **b** direction and one Na^+ ion on a crystallographic twofold axis in the **c** direction. All anions have approximate C_{3v} symmetry, and their molecular parameters are within the expected ranges. Two Na^+ ions are each surrounded by six O atoms, forming distorted octahedral configurations with Na–O distances ranging from 2.276 (2) to 2.669 (1) Å, whereas the third Na^+ is surrounded by eight O atoms with Na–O distances ranging from 2.318 (1) to 3.099 (1) Å.

Introduction

Attempts to crystallize the methanesulfonate salt of an antischistosomal drug, IA-4 *N*-oxide (Bueding, Fisher & Bruce, 1973), containing a chlorobenzothiopyranoindazole fragment (Patterson, Capell & Walker, 1960), have led to an accidental preparation of colorless, thin-plate crystals which were subsequently characterized by X-ray analysis as the sodium salt of methanesulfonic acid. The only reported crystal structure of a Group Ia-metal salt of methanesulfonic acid was that of cesium (Brandon & Brown, 1967), whereas two structures containing CH_3SO_3^- anions have previously been determined in our laboratory: hycanthone methanesulfonate (Wei & Einstein, 1978) and the methanesulfonate of a molecule similar to hycanthone, denoted IA-4 (Wei, 1981). Results of the present study provide additional accurate information concerning molecular parameters of the CH_3SO_3^- anions as well as O-coordination spheres about Na^+ ions.

Experimental

To a yellowish solution of 19 mg of IA-4 *N*-oxide methanesulfonate in 0.5 ml of 50% ethanol, a small amount of 0.1 *M* NaOH was added to pH 6.3 whereupon a few grains of colorless, thin-plate crystals were obtained along with greyish amorphous powder. Preliminary cell parameters and systematic absences were determined from Weissenberg and precession photographs. 12 strong reflections in the 2θ range of 126–133° were centered with an Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968) by use of Ni-filtered Cu $K\alpha_1$ ($\lambda = 1.54051$ Å) radiation, and the cell parameters were refined by the least-squares method. Additional crystal data are given in Table 1.

A crystal of dimensions 0.55 × 0.27 × 0.02 mm was glued on the tip of a thin glass fiber with the longest dimension, corresponding to the *c* axis, nearly parallel to the φ axis of the diffractometer. The maximum

Table 1. Additional crystal and intensity-collection data

Systematic absences: $0kl, k = 2n + 1; hk0, h = 2n + 1$		
Space group: <i>Pbma</i> or <i>Pb2₁a</i> [corresponding to international symbol <i>Pbcm</i> (D_{2h}^8 , No. 57) or <i>Pca2₁</i> (C_{2v}^8 , No. 29)]		
Radiation: Cu $K\alpha$	Total background counting time	24–96 s ^b
Take-off angle: 3°	Number of unique nonzero reflections	1953
Scan type: θ – 2θ step scan	Number of reflections used in refinement	1850 ^c
2θ limit: 136°	Number of variables	178
2θ step size: 0.05°	Data-to-variable ratio	10.4
Time per step: 2–4 s		
Scan width: 1.5–1.7° ^a		

^a The width of the $\alpha_1 - \alpha_2$ separation was added to these values.

^b Backgrounds were measured at the beginning and end of each scan. The longer times were used for higher 2θ ranges.

^c Criteria used were $F_o^2 \geq \sigma(F_o^2)$ and $|\Delta F^2| \leq 4\sigma(F_o^2)$.

mosaic spread of the crystal was estimated to be 0.4°. The intensities were measured up to a 2θ value of 136° (equivalent to a minimum spacing of 0.83 Å) with Ni-filtered Cu $K\alpha$ radiation at 40 kV and 18 mA. During the course of data collection, intensities of standard reflections fluctuated within ±2%. Details of the intensity collection are also given in Table 1. Absorption corrections were made by the method of Busing & Levy (1957), and weights (*w*) used in the refinement of the structure [in which some reflections were not included (see Table 1)] were reciprocals of variances $\sigma^2(F_o^2)$, which were estimated according to the empirical expression routinely employed in our laboratory (Wei & Einstein, 1978).

Solution and refinement of the structure

At the beginning of the analysis, the actual structural formula was unknown. Interpretation of a three-dimensional Patterson function, calculated by the use of a fast-Fourier routine (Levy, 1977), in terms of a possible fused four-ring system containing one S and one Cl atom, as in the case of the IA-4 cation (Wei, 1981), was unsuccessful. Instead, three heavy atoms were initially located and were subsequently interpreted as S atoms of three methanesulfonate anions, each of which was electrically balanced by one Na^+ cation. The assumption of a mirror plane in the **b** direction, leading to the choice of the centrosymmetric space group *Pbma*, is consistent with the average values of 1.018 and 0.777 for $|E^2 - 1|$ and $|E|$, respectively [theoretical values for centrosymmetric: 0.968, 0.798; for non-centrosymmetric: 0.736, 0.886 (Karle, Dragonette & Brenner, 1965)].

All C and O atoms of the methanesulfonate anions were located from a difference Fourier synthesis. The isotropic refinement of the structure, comprising 17 independent non-H atoms, by the use of a block-

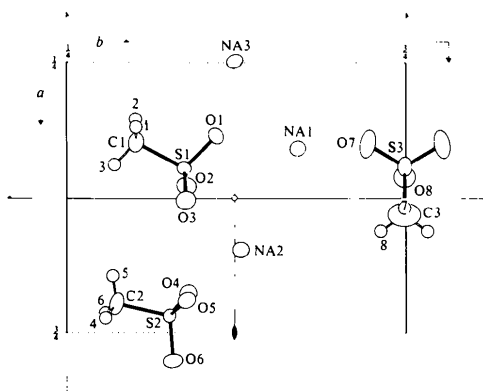


Fig. 1. Numbering scheme and arrangements of the independent molecules in an asymmetric unit. The CH_3SO_3^- anion, associated with S(3), and Na(3) are at special positions. This and the following figures were prepared with the program ORTEP II (Johnson, 1976).

diagonal program [local modification by J. R. Einstein of the program of Shiono (1971)] gave an $R(F)$ value of 0.084, which was lowered to 0.066 after several cycles of anisotropic refinement. The subsequent difference Fourier synthesis yielded the positions for the eight independent H atoms. When these H atoms were included in the refinement, with fixed positions and isotropic thermal parameters, the $R(F)$ value dropped to 0.045. As can be seen in Fig. 1, which shows the numbering scheme and arrangements of the independent molecules in an asymmetric unit, one CH_3SO_3^- anion associated with S(3) is related to itself by a mirror plane at $y = \frac{3}{4}$, and Na(3) is on a twofold axis at $x = \frac{1}{4}$ and $y = \frac{1}{2}$.

The intensity data were reprocessed with the correct linear absorption coefficient, and refinements based on F^2 were resumed with the full-matrix least-squares program ORXFLS4 (Busing, Martin & Levy, 1962). An isotropic extinction parameter and, later, anisotropic extinction parameters of type I (Coppens & Hamilton, 1970) were incorporated. It was necessary to reset a negative Z'_{11} term to zero, although its value was not significantly different from zero [-0.0001 (8) on the last cycle]. At the end of the refinement, $R(F)$, $R(F^2)$, and $R_w(F^2)$ [the last term defined as $(\sum w|F_o^2 - sF_c^2|^2 / \sum wF_o^4)^{1/2}$, where s is a scale factor] had values of 0.024, 0.041, and 0.063 respectively, for 1850 reflections with $F_o^2 \geq \sigma(F_o^2)$ and $|F_o^2 - sF_c^2| \leq 4\sigma(F_o^2)$. When all 1953 reflections were included, the $R(F)$ value was 0.027. Positional and thermal parameter shifts for the non-H atoms in the last cycle of the refinement were all less than 2% of the corresponding e.s.d.'s, whereas maximum shifts in H parameters were 6% of the corresponding e.s.d.'s. The anisotropic extinction parameters (arbitrarily assigned orthorhombic symmetry) were $Z'_{11} = 0.0000$ (8), $Z'_{22} = 0.024$ (5),

Table 2. Positional and equivalent isotropic thermal parameters for non-H atoms

The e.s.d.'s of the last significant figures are given in parentheses in all tables and in the text. Equivalent isotropic thermal parameters, B_{eq} , were calculated by the relation $B_{\text{eq}} = \frac{1}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2)$ (Hamilton, 1959).

	$x (\times 10^5)$	$y (\times 10^5)$	$z (\times 10^4)$	$B_{\text{eq}} (\text{\AA}^2)$
S(1)	44750 (2)	42643 (2)	2200 (1)	1.51 (1)
C(1)	40069 (11)	35586 (8)	2424 (3)	2.70 (4)
O(1)	38784 (7)	47280 (5)	2588 (2)	2.35 (3)
O(2)	48047 (6)	43010 (5)	-195 (2)	2.52 (3)
O(3)	50732 (6)	42929 (5)	4045 (2)	2.83 (3)
S(2)	72519 (2)	40658 (2)	2685 (1)	1.43 (1)
C(2)	70307 (14)	32886 (8)	2705 (4)	3.07 (5)
O(4)	68410 (6)	43376 (5)	662 (2)	2.51 (3)
O(5)	69601 (6)	43186 (5)	4924 (2)	2.29 (3)
O(6)	80963 (7)	41202 (6)	2467 (2)	2.74 (3)
S(3)	44167 (3)	75000	1549 (1)	2.27 (1)
C(3)	53152 (26)	75000	3073 (7)	5.77 (12)
O(7)	40061 (10)	69577 (6)	2297 (3)	4.25 (4)
O(8)	46105 (10)	75000	-962 (3)	3.25 (4)
Na(1)	40974 (3)	59276 (3)	2465 (1)	1.96 (2)
Na(2)	59939 (4)	51056 (3)	2887 (1)	2.30 (2)
Na(3)	25000	50000	2181 (1)	1.95 (2)

Table 3. Positional ($\times 10^3$) and isotropic thermal parameters for H atoms

	x	y	z	$B (\text{\AA}^2)$
H(1)	373 (1)	356 (1)	406 (4)	3.0 (4)
H(2)	359 (1)	355 (1)	102 (4)	3.8 (5)
H(3)	442 (1)	324 (1)	217 (4)	4.1 (5)
H(4)	730 (2)	313 (1)	410 (5)	5.8 (7)
H(5)	651 (1)	323 (1)	273 (3)	3.5 (5)
H(6)	721 (1)	313 (1)	126 (5)	5.0 (6)
H(7)	519 (2)	750	454 (8)	6.5 (10)
H(8)	563 (2)	716 (2)	255 (5)	8.4 (10)

and $Z'_{33} = 0.00024$ (6). A final difference synthesis showed peaks ranging from 0.4 to -0.4 e \AA^{-3} . Scattering factors used were those of Ibers (1962) for C, O, Na^+ , and S; those of Stewart, Davidson & Simpson (1965) for H. The real and imaginary corrections, $f' = 0.129$ and 0.319 and $f'' = 0.124$ and 0.557 , were employed for Na and S, respectively (Cromer, 1974).

The final atomic parameters are given in Table 2 for non-H atoms and in Table 3 for H atoms. Some anisotropic thermal parameters were constrained to be zero by symmetry (Peterse & Palm, 1966) for non-H atoms at special positions.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36056 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

The structure consists of CH_3SO_3^- anions linked to Na^+ ions in a three-dimensional network. Bond distances and bond angles, calculated by program *ORFFE4* (Busing, Martin & Levy, 1964), for three independent anions are given in Table 4, and their configurations as viewed down the S—C bond directions are shown in

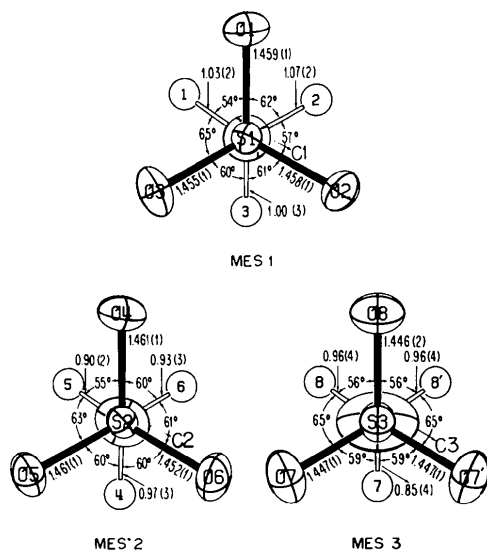


Fig. 2. Configurations of three methanesulfonate anions as viewed down the S—C directions. S—O and C—H distances, and O—S—C—H torsion angles are shown. O(7') and H(8') are related to O(7) and H(8) by the mirror plane passing through S(3), C(3), O(8), and H(7) atoms. E.s.d.'s for the O—S—C—H torsion angles are 1° for MES (1), $1-2^\circ$ for MES (2), and 2° for MES (3) with exceptions of 0.08° for O(7)—S(3)—C(3)—H(7) and O(7')—S(3)—C(3)—H(7).

Table 4. Bond distances (Å) and bond angles ($^\circ$) of CH_3SO_3^- anions in NaCH_3SO_3

MES (1)		MES (2)		MES (3)	
S(1)—C(1)	1.752 (2)	S(2)—C(2)	1.753 (2)	S(3)—C(3)	1.756 (4)
S(1)—O(1)	1.459 (1)	S(2)—O(4)	1.461 (1)	S(3)—O(8)	1.446 (2)
S(1)—O(2)	1.458 (1)	S(2)—O(5)	1.461 (1)	S(3)—O(7)	1.447 (1)
S(1)—O(3)	1.455 (1)	S(2)—O(6)	1.452 (1)	[S(3)—O(7')	1.447 (1)]
mean	1.457 (1)	mean	1.458 (1)	mean	1.447 (1)
MES (1)		MES (2)		MES (3)	
C(1)—S(1)—O(1)	106.97 (8)	C(2)—S(2)—O(4)	107.54 (8)	C(3)—S(3)—O(7)	106.4 (1)
C(1)—S(1)—O(2)	106.93 (8)	C(2)—S(2)—O(5)	107.06 (8)	[C(3)—S(3)—O(7')	106.4 (1)]
C(1)—S(1)—O(3)	107.91 (8)	C(2)—S(2)—O(6)	107.16 (9)	C(3)—S(3)—O(8)	105.9 (2)
mean	107.27 (5)	mean	107.25 (5)	mean	106.2 (1)
O(1)—S(1)—O(2)	111.62 (6)	O(4)—S(2)—O(5)	110.30 (7)	O(8)—S(3)—O(7)	113.14 (7)
O(1)—S(1)—O(3)	110.70 (7)	O(4)—S(2)—O(6)	112.19 (7)	[O(8)—S(3)—O(7')	113.14 (7)]
O(2)—S(1)—O(3)	112.41 (7)	O(5)—S(2)—O(6)	112.29 (7)	O(7)—S(3)—O(7')	111.3 (1)
mean	111.58 (4)	mean	111.59 (4)	mean	112.5 (1)

O(7') and H(8') are related to O(7) and H(8) by the mirror plane at $y = \frac{1}{2}$. Distances and angles involving O(7'), enclosed in brackets, are included for averaging. H—C—S angles are in the range $104-111^\circ$ with e.s.d.'s of $1-3^\circ$, and average 107° . H—C—H angles are in the range $103-116^\circ$ with e.s.d.'s of $2-5^\circ$, and average 112° .

Fig. 2, with some bond lengths and O—S—C—H torsion angles (MES designates methanesulfonate). In the refinement of the structure, the negative charge was assumed to be uniformly distributed on O atoms, *i.e.* the atomic scattering factor used was the sum of $\frac{2}{3}f(\text{O})$ and $\frac{1}{3}f(\text{O}^-)$. Hence, the resulting S—O distances and C—S—O and O—S—O bond angles are assumed to be equivalent. Of the three independent CH_3SO_3^- anions in this structure, MES(1) and MES(2) are in general positions, and MES(3) is at a special position with S(3), C(3), O(8), H(7) atoms on a crystallographic mirror plane.*

* Atoms C(3) and O(7) have particularly large thermal vibrations. The maximum r.m.s. thermal displacement along any direction is $0.346(6)$ Å for the former and $0.295(2)$ Å for the latter, while the corresponding values for the other 15 non-H atoms range from $0.145(1)$ to $0.230(2)$ Å. In an attempt to investigate possible anharmonic vibrations, third-order cumulants of the probability functions for thermal motions (Johnson, 1969) of atoms S(3), C(3), and O(7) were incorporated in the refinement [22 additional parameters, given the symmetry restrictions (Johnson & Levy, 1974)], resulting in an $R_w(F^2)$ value of 0.0829 for all 1953 reflections. Since the corresponding $R_w(F^2)$ value from the regular refinement was 0.0861 , the R -value ratio was 1.039 . Interpolation (Pawley, 1970) in the Hamilton tables (Hamilton, 1965) for $a = 0.001$ gave an $\mathcal{A}_{b,n-m,a}$ value of 1.014 , where $b = 22$ and $n - m = 1775$. Hence, the hypothesis that there are no anharmonic thermal vibrations for S(3), C(3), and O(7) could be rejected at the 99.9% confidence level. Examination of the subsequent skew density distribution for these atoms revealed that O(7) had a crescent shape perpendicular to the S(3)—O(7) bond, while S(3) had an anharmonic rocking motion toward C(3) and O(8) and away from O(7) and O(7'). The inclusion of third-order cumulants in a least-squares refinement results in atomic positions at the means and not the modes of the probability functions, yielding incorrect bond lengths (Johnson, 1969). Therefore, the results presented in this paper are based on those obtained from the conventional refinement.

Table 5. S—C and S—O distances (Å) and C—S—O and O—S—O bond angles (°) in NaCH₃SO₃ and related compounds

Compound	S—C	S—O	C—S—O	O—S—O	Reference
Potassium methanedisulfonate	1.770 (7)	1.461 (5)	105.3 (3)	113.3 (3)	Truter (1962)
Cesium methanesulfonate	1.80 (3)	1.45 (1)	106.9 (7)	111.9 (6)	Brandon & Brown (1967)
(-)-1- <i>tert</i> -Butylamino-3-(2-cyclopentyl-phenoxy)propan-2-ol methanesulfonate	1.79 (1)	1.413 (5)	107.7 (4)	111.2 (4)	Kobelt & Paulus (1974)
Hycanthon methanesulfonate	1.749 (3)	1.446 (1)	106.2 (1)	112.5 (1)	Wei & Einstein (1978)
IA-4 methanesulfonate	1.746 (5)	1.445 (1)	105.9 (2)	112.8 (2)	Wei (1981)
Sodium methanesulfonate	1.754 (2)	1.454 (1)	106.91 (4)	111.89 (4)	This work
Weighted average*	1.754 (2)	1.448 (1)	106.77 (4)	112.01 (4)	

* The weighted average of a parameter P_{av} is defined as $P_{av} = (\sum P_i/\sigma_i^2)/(\sum 1/\sigma_i^2)$, and its e.s.d. is defined as $[(1/(\sum 1/\sigma_i^2))]^{1/2}$.

The three S—C distances in this structure range from 1.752 (2) Å for S(1)—C(1) to 1.756 (4) Å for S(3)—C(3). It was proposed by Cruickshank (1961) that the C atom in the CH₃SO₃⁻ anion should have no *p* orbital for π -bonding with 3*d* orbitals of S, so that the S—C bond was expected to be a pure single bond of length at least 1.77 Å. Our observed S—C distances are in close accordance with this proposition. The S—O distances and C—S—O and O—S—O bond angles for the three MES groups are closely similar. In Table 5, bond lengths and angles are given for six related compounds. In each case [except for potassium methanedisulfonate (Truter, 1962)], the CH₃SO₃⁻ anion closely conforms to C_{3v} symmetry. In the present structure, O atoms do not participate in hydrogen bonding as in the cases of hycanthon methanesulfonate (Wei & Einstein, 1978) and IA-4 methanesulfonate (Wei, 1981). Still, the overall agreement of the molecular parameters in Table 5 is acceptable.

In many structures containing RSO₃ groups where R is bonded through a C atom (cited by Brandon & Brown, 1967; summarized by Arora & Sundaralingam, 1971; Cody & Hazel, 1977), the C—S—O angles are smaller and O—S—O angles are larger than a regular tetrahedral angle because of mutual repulsion of the charged O atoms. Similar phenomena were observed for tetraaquabis(methanesulfonato)copper(II) complex (Charbonnier, Faure & Loiseleur, 1975) and compounds containing CF₃SO₃⁻ anions, including ammonium trifluoromethanesulfonate (Gänswein & Brauer, 1975), trifluoromethanesulfonic acid monohydrate (Spencer & Lundgren, 1973), trifluoromethanesulfonic acid dihydrate (Delaplane, Lundgren & Olovsson, 1975*a*), and trifluoromethanesulfonic acid hemihydrate (Delaplane, Lundgren & Olovsson, 1975*b*). Structural results obtained for the six compounds cited in Table 5 are consistent with these observations: the weighted average deviations from 109° 28' are -2.70 (4)° for C—S—O and 2.54 (4)° for O—S—O angles. These deviations are nearly opposite in each case, so that the sum of the average C—S—O and O—S—O angles for an

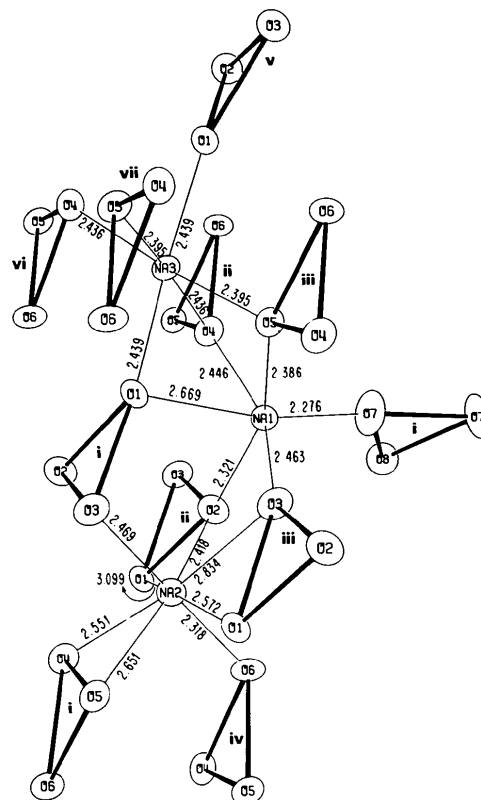


Fig. 3. Coordinations about three Na⁺ ions. E.s.d.'s of Na—O distances are all 0.001 Å except for Na(1)—O(7), for which the e.s.d. is 0.002 Å. Symmetry code: (i) *x*, *y*, *z*; (ii) 1 - *x*, 1 - *y*, -*z*; (iii) 1 - *x*, 1 - *y*, 1 + *z*; (iv) 1½ - *x*, 1 - *y*, *z*; (v) ½ - *x*, 1 - *y*, *z*; (vi) -½ + *x*, *y*, -*z*; and (vii) -½ - *x*, *y*, 1 - *z*.

individual anion ranges from 218.6 (4) to 218.9 (6)°, approximately double the regular tetrahedral angle.

Coordination geometries about the three metal ions are depicted in Fig. 3. Within 3.5 Å around Na(1), six O atoms, each belonging to a different methanesulfonate group, form a coordination sphere with Na—O distances ranging from 2.276 (2) to

2.669 (1) Å. Similarly, Na(3) is coordinated within a radius of 3.4 Å by three pairs of twofold-related O atoms, each being furnished by a different methanesulfonate group. The Na(3)—O distances range from 2.395 (1) to 2.439 (1) Å. In these two cases, coordination around Na⁺ ions is distorted octahedral, and unmistakably sixfold with average Na—O distances of 2.427 (1) and 2.423 (1) Å for Na(1) and Na(3), respectively. These values agree with the average Na—O distance of 2.44 Å tabulated for six-coordination of O about Na (Ondik & Smith, 1962). The Na(2) coordination is distinctly different from that for Na(1) and Na(3) and is less clear-cut in terms of its coordination number. The coordination sphere is made up of six O atoms, two each from three methanesulfonate groups in bifurcated interactions, plus two additional O atoms from two other methanesulfonate groups. The six nearest O atoms are less than 2.66 Å from the Na(2)⁺ ion, and the other O atoms are at distances of 2.834 (1) and 3.099 (1) Å. If only the seven shortest contacts are considered, the average Na—O distance is 2.545 (1) Å, again closely parallel to the value of 2.53 Å given for seven-coordination (Ondik & Smith, 1962). In light of chemical and geometrical considerations, however, the coordination about Na(2) is best described as eightfold.

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