THE CRYSTAL AND MOLECULAR STRUCTURE OF SCANDIUM FORMATE

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The structure of $Sc(HCOO)_3$ was refined up to $R = 0.046$. The substance crystallizes in the monoclinic system, space group $P2_1/c$, $a = 10.340(2)$, $b = 6.631(1)$, $c = 9.027(2)$ Å, $\beta = 98.11(2)°$, $Z = 4$. Scandium atoms are placed in the two symmetrically non-equivalent centres of symmetry thus forming alternating layers parallel to the plane of b, c. All formate oxygens are coordinated to Sc atoms thus forming a three-dimensional net with octahedral coordination of both independent Sc atoms. C—H bonds are oriented in between the nearest oxygens of neighbouring formate groups, but only one contact is sufficiently short to be denoted as the C—H⋯O hydrogen bond. IR and Raman spectra seem to confirm the differences between formate anions.

The crystal and molecular structure of $Sc(HCOO)_3$ was determined by Guseinova, Antsishkina and Porai-Koshits[1] in 1968 with a high R value of 0.20 using 832 measured reflexions. Temperature factors were supposed to be isotropic and H atoms were not found. A deeper analysis of the crystal structure of $Sc(HCOO)_3$ with $R = 0.04$ for 1 774 reflexions, anisotropic temperature factors for non-H atoms and isotropically refined H atoms is presented in this paper. The atomic labels have been left as in ref.[1] for reader's convenience.

EXPERIMENTAL

Preparation of Single Crystal

The scandium formate was prepared by dissolution of Sc_2O_3 (impurities in ppm: Si 15, P 10, Na 6.5, Th 42, Y, Fe, Mg, Ca 1.5, all other elements below the detection limit of ICP emission analysis) in redistilled, 50% formic acid and isolated by crystallization. Large single crystals (up to 10 mm) were grown in an isothermal crystallizer with reflux of solvent[2] from a solution containing 25% of $Sc(HCOO)_3$ and 3% of $HCOOH$ in redistilled water. The much smaller single crystals for X-ray diffraction were picked up as parasites during the growth of the large crystals.

Optical Crystallography

Habitus of two shape variants of the large single crystals was measured with an optical two-
-circle reflecting goniometer (Stoe and Heidelberg). Two shape variants are generally observed
among scandium formate single crystals grown isothermally from a seed under minimum space
limiting conditions. Both these variants (platelet-like and column-like crystals) are shown in
Fig. 1. Indexing of crystal faces corresponds to monoclinic syngony. The gnomonic projection
of crystal faces (Fig. 2) corresponds to the habitus, with point group *2/m*.

IR Spectroscopy

IR spectra were recorded with a Perkin–Elmer 325 spectrometer in KBr discs in the range from
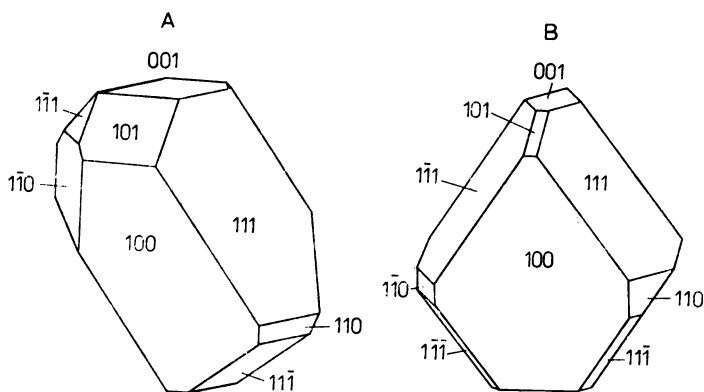4 000 to 200 cm^{-1}.

FIG. 1

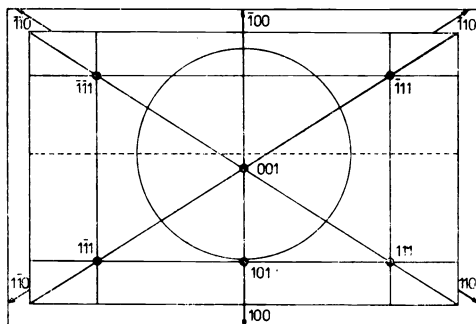Habitus of single crystals of Sc(HCOO)$_3$, A column like, B platelet-like crystals

FIG. 2

Gnomonic projection of the crystal faces

Crystallographic Data

The lattice parameters $a = 10.340(2)$, $b = 6.631(1)$, $c = 9.027(2)$ Å, $\beta = 98.11(2)°$ were refined by the least-squares method from 20 reflexions (with 2Θ from $19°$ to $35°$) centered on Syntex P2$_1$ diffractometer (MoK$_\alpha$ radiation, $\lambda = 71.069$ pm). The crystal density measured by flotation $D_o = 1.94$ Mg m^{-3} is in good agreement with $D_c = 1.95$ Mg m^{-3} calculated for four formula units in the unit cell. The systematic absences indicated the $P2_1/c$ space group. The ψ scan showed that several systematically absent reflexions were considerably influenced by multiple scattering (variations of intensities from 0 to 15 e.s.d.s). A number of 365 from the total number of 2 139 symmetrically independent reflexions with $2\Theta < 65°$ measured by $\Theta - 2\Theta$ scan were classified as unobserved using the criterion $I < 1.96\sigma(I)$. Neither the extinction nor the absorption correction ($\mu(MoK_\alpha) = 1.19$ mm^{-1}, $r \approx 0.2$ mm) were applied. No significant decrease in three reference intensities was observed during the measurement. Eight strongest reflexions were measured using a lower anode current.

Structure Determination and Refinement

Positions of all non-H atoms were uniquely shown by MULTAN 80 program[3]. The structure was refined by full-matrix least squares using the SHELX 76 program[4]. The minimized function was $\sum w\Delta^2$, where $w = [\sigma_F^2 + (0.028F)^2]^{-1}$, and $\Delta = ||F_o| - |F_c||$. The unobserved reflexions were not used in the refinement. Nonhydrogen atoms were refined with anisotropic and hydrogen atoms (localized from a difference map) with isotropic temperature factors until all shifts were lower than 0.1 of the corresponding e.s.d.'s and $R = \sum\Delta/\sum|F_o| = 0.046$, $Rw = \sum w\Delta^2/\sum w|F_o|^2 = 0.061$ for 1 774 observed reflexions and 44 refined parameters. The peaks on the final difference map (less than 700 e nm^{-3}) could not be interpreted uniquely as lone electron pairs, probably because the data were not corrected for absorption. The geometry was calculated by the PARST (ref.[5]) and IMC (ref.[6]) programs. Final atomic coordinates are given in Tables I and II.

DISCUSSION

Scandium atoms are placed at the two non-equivalent centers of symmetry (Fig. 3), thus forming alternating layers (parallel to the plane of the lattice vectors $\boldsymbol{b}$, $\boldsymbol{c}$) of Sc1 atoms at $x = 0, 1, 2$, etc., and Sc2 atoms at $1/2$, $3/2$, etc. The Sc2 atoms are shifted by the vector $(1/2, 1/2, 0)$ with respect to Sc1 atoms. The centers of symmetry $(0, 1/2, 0)$ and $(1/2, 1/2, 1/2)$ remain unoccupied. The formate groups O1— —C1—O3 form infinite helices with Sc2 atoms around the screw axes at $x = 0$, $z = (2n + 1)/4$. Analogically, the neighbouring Sc1 atoms shifted by the vector $(0, 1/2, 1/2)$ are bonded together by O5—C3—O6 groups symmetrically related by screw axes at $x = 1/2$, $z = 2n + 1/4$. However, the inifinite helices between Sc2 atoms are wider than the helices between Sc1 atoms, probably because of the influence of the H-bond C2—H2···O6 (Fig. 3). The neighbouring right and left-handed helices have common scandium atoms thus forming alternating layers. The layers containing Sc1 atoms are bonded together with the layers Sc2 by infinite —Sc1— —O2—C2—O4—Sc2— chains with the mean directions $(1, 1, 0)$ and $1, -1, 0)$ for symmetrically related chains.

Coordination of Sc *Atoms*

Both Sc atoms are octahedrally coordinated to three symmetrically independent oxygens and three of their centrosymmetric counterparts, so that each octahedron is fully described by three O—Sc—O angles and Sc—O distances (Fig. 3). Thus, the environment of Sc2 is formed by three almost perpendicular planes O4, Sc2, O5 (iv); O6, Sc2, O5 (iv); O4, Sc2, O6. Codes of equivalent positions are given in Table III. Analogically, Sc1 lies at the intersection of the three almost perpendicular planes O1, Sc1, O2; O1, Sc1, O3 (iii); O2, Sc1, O3 (iii). The Sc2 atoms lie almost in the plane O2, C2, O4 (deviation 0·003(5) Å, torsion angle O2—C2—O4—Sc2 179·8(3)°). The deviation of Sc2 from the plane O5, C3, O6 is statistically significant but small, 0·088(3) Å. The torsion angles are O5—C3—O6—Sc2 −175·9(2)° and O6—C3—

TABLE I

Refined coordinates of $Sc(HCOO)_3$ with their estimated standard deviations $(.10^4)$ and the equivalent isotropic thermal parameters $(.10^4 \text{ Å}^2)$; $U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)/3$

Atom	x/a	y/b	z/c	U_{eq}
Sc1	0(0)	0(0)	0(0)	208(3)
Sc2	5 000(0)	5 000(0)	0(0)	246(3)
C1	660(2)	9 078(3)	3 421(2)	266(10)
C2	2 859(4)	1 950(6)	767(5)	773(23)
C3	3 602(3)	7 079(5)	2 494(3)	456(14)
O1	15(2)	8 872(3)	2 169(2)	375(9)
O2	1 921(2)	902(3)	484(2)	476(11)
O3	667(2)	7 859(2)	4 481(2)	346(8)
O4	3 451(2)	3 016(3)	69(2)	479(11)
O5	3 692(2)	8 202(3)	3 600(2)	452(10)
O6	4 519(2)	6 579(3)	1 830(2)	483(11)

TABLE II

Refined coordinates of H atoms with their e.s.d.'s $(.10^3)$ and temperature parameters $U_{iso}(.10^3 \text{ Å}^2)$

Atom	x/a	y/b	z/c	U_{iso}
H1	127(3)	23(4)	378(3)	36(8)
H2	328(6)	201(11)	214(7)	164(29)
H3	260(4)	653(6)	203(5)	67(11)

—O5—Sc2 3·9(6)°. The position of the formate planes to Sc1 are different, as seen from the respective torsion angles O3—C1—O1—Sc1 $-40·0(3)°$, O1—C1—O3—Sc1 $7·7(4)°$, O4—C2—O2—Sc1 $-78·0(9)°$. The deviation of Sc1 from O3, C1, O1 plane is $0·17(1)$ Å and the deviation from O4, C2, O2 plane is $0·66(1)$ Å. Coordination octahedra around Sc1 and Sc2 are shown in Fig. 4.
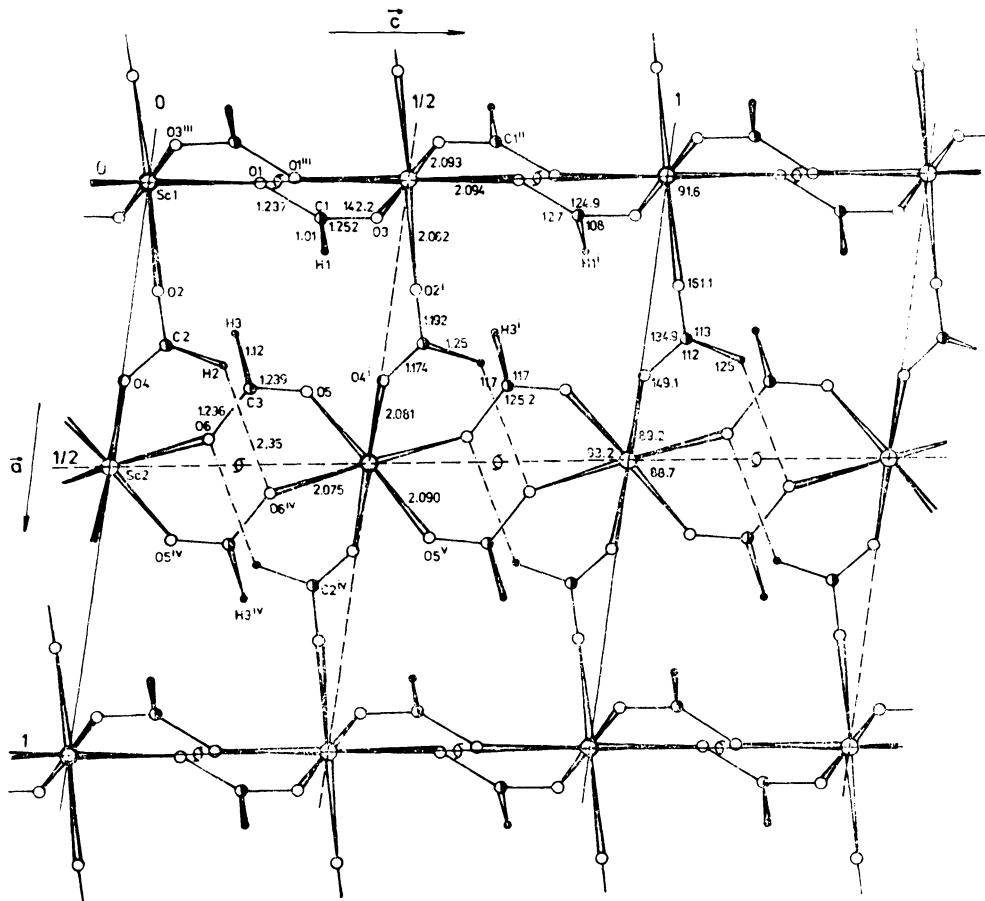

FIG. 3

A view of scandium formate along the b axis. Sc2 atoms in horizontal lines are placed alternately at the heights $y = 0$, $1/2$, $1, \ldots$ and Sc1 atoms at $y = 1/2$, 1, $3/2, \ldots$. The e.s.d.'s of bond distances and angles are in ranges: Sc–O $0·001-0·002$ Å, O–Sc–O $0·1°$, C–O $0·003-0·005$ Å. Sc–O–C $0·2-0·3°$, C–H $0·04-0·06$ Å, O–C–H $2·0-3·0°$. Codes of equivalent positions are given in Table III

Hydrogen Atoms

X-ray diffraction localizes the centers of electron density and not the positions of atomic nuclei. Centers of electron density of H atoms are significantly shifted with respect to the positions of protons in dependence on the character of the bond. The average distance of C—H1 and C—H3 is $1·06(4)$ Å and the average U_{iso} $5(1)$. 10^2 Å^2; however, H2, which forms a hydrogen bond to O6 (iv), has a center of electron

TABLE III

Symmetrically equivalent positions used in text and Fig. 3

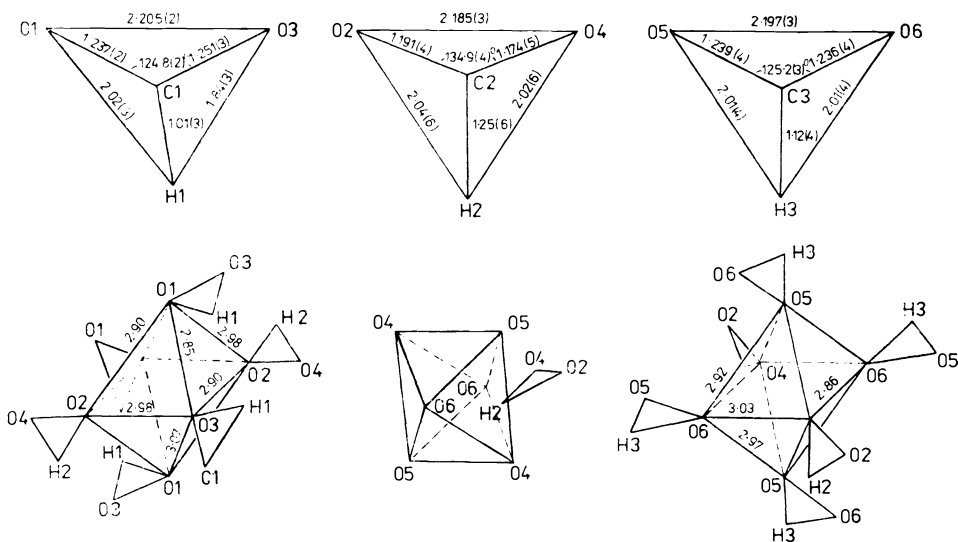| (i)	$x, 1/2 - y, 1/2 + z$	(vi)	$x,\quad y - 1,\qquad z$
(ii)	$-x,\quad 1 - y,\quad 1 - z$	(vii)	$1 - x, 1/2 + y, 1/2 - z$
(iii)	$-x, 1/2 + y, 1/2 - z$	(viii)	$x, 3/2 - y, z - 1/2$
(iv)	$1 - x, y - 1/2, 1/2 - z$	(ix)	$-x, y - 1/2, 1/2 - z$
(v)	$x, 3/2 - y, 1/2 + z$	(x)	$x,\quad 1 + y,\qquad z$

FIG. 4

The three crystallographically nonequivalent formate anions as seen by X-ray diffraction, co-ordination of these anions in the two different coordination polyhedra octahedra around scandium atoms, including possible H-bridge interaction of the H2 atom with the neighbouring octahedron

density 1·25(6) Å from C2 and high $U_{iso} = 16(3) . 10^2 \text{ Å}^2$. The deviations of H atoms from the corresponding O, C, O planes are within units of e.s.d. s.

The hydrogen atoms have a rather different environment, though all are surrounded by six oxygen neighbours, in addition to those from their own formate anion. The H1 is directed into a cavity formed by oxygens at distances: 2·66(5), 2·83(3), 2·87(5), 2·99(3), 3·02(4) and 3·17(4) Å to the O4(i), O1(ix), O5(vi), O3(ii), O2(i) and O2, respectively (2·92 ± 18 Å on the average). The observed C1—H1(x) distance is 1·01(3) Å.

The H3 atom enters only into weak interactions outside the formate anion, as follows from the H3···O distances: 2·86(4), 3·13(4), 3·25(4), 3·39(4), 3·44(4) and 3·67(4) Å to the O3(viii), O4, O2(x), O1(ix), O5(viii) and O2(i), respectively (3·29 ± 0·28 Å on the average). The electron density centre of the H3 atom is 1·12(4) Å from the corresponding carbon atom.

The strongest interactions are shown by H2, with rather short distances to three of the six neighbouring oxygens, 2·35(6), 2·62(6) and 2·85(6) Å, to the O6(iv), O4(i), and O2(i), respectively. The more distant oxygens O6, O1(ix) and O2(i) are 3·32(7), 3·76(7) and 3·77(7) Å apart, respectively. The shift of the electron density centre of H2 up to the distance 1·25(6) Å from the carbon atom, the short H2···O6(iv) distance (2·35 Å), C2···O6(iv) 3·233(4) Å and the C2—H2···O6(iv) angle (125(4)°) all speak in favour of a distinct hydrogen bond interaction.

Formate Anions

The pronounced differences in positions of electron density centres of the hydrogen atoms among the three crystallographically nonequivalent formate anions are to some extent reflected in a variation of the corresponding carbon–oxygen bonds (Fig. 5). While the carbon–oxygen distances in the anions formed by C1 and C3 may be in the first approach considered as comparable, a significant shortening of both C2—O2 and C2—O4 bonds is observed, as H2 is situated further from the carbon atom in the formate anion. The decrease in the C2—H2 bond strength then increases the bond order between carbon and both oxygens and shortens the bonds. Moreover, the enhanced order of the carbon–oxygen bonds opens the O2—C2—O4 angle by some 10° in comparison with the O1—C1—O3 and O5—O3—O6 angles.

Vibrational Spectrum

To estimate whether the shifts in the position of electron density centres are accompanied by shifts of the nuclei and whether the resulted change in bond energy is significant, the IR vibrational spectrum of $Sc(HCOO)_3$ was measured. An analysis of normal vibrational modes of an isolated formate anion (point group C_{2v}) predicts 3 normal modes in the A_1 symmetry species, 1 normal mode in the B_2 symmetry

TABLE IV

Site and factor group analysis of irregular formate anion (point group C_s) in the crystal structure Sc(HCOO)$_3$ space group C_{2h}^5, site group of the anion C_1)

Group symbol	G_M	$\geq$	G_s	$\leq$	G_F
Point group	C_s		C_1		C_{2h}
Order	2		1		4
Vibration modes	$5A'$(IR, RA)		$6A$		$6(A_g + B_g)$ (RA)
	A''(IR, RA)				$6(A_u + B_u)$ (IR)

TABLE V

Site and factor group analysis of regular formate anion (point group C_{2v}) in the crystal structure of Sc(HCOO)$_3$ with space group C_{2h}^5, site group of the formate C_1

Group symbol	G_M	$\geq$	G_s	$\leq$	G_F
Point group	C_{2v}		C_1		C_{2h}
Order	4		1		4
Vibration modes	$3A_1$(IR, RA)				$6(A_g + B_g)$ (RA)
	$2B_1$(IR, RA)		$6A$		
	B_2(IR, RA)				$6(A_u + B_u)$ (IR)

TABLE VI

The fundamental vibration modes of the formate ions in Sc(HCOO)$_3$ structure

Assignment	Description	Obs. frequency, cm^{-1}	Type	Note
ν_1	C—H stretch	2 880	A_1	formate C3
		2 925		formate C1
		2 765		formate C2
ν_2	symmetric OCO stretch	1 380	A_1	
ν_3	symmetric OCO deformation	788	A_1	formate C1, C3
		800		formate C2
ν_4	asymmetric OCO stretch	1 570	B_1	
ν_5	asymmetric OCO deformation	1 400	B_1	traces of NO$_3^-$
ν_6	out-of-plane deformation	1 060	B_2	traces of NO$_3^-$

species and 2 normal modes in the B_1 symmetry species, all of them active both in infrared absorption and in Raman scattering. According to the site group and factor group analysis (shown in Tables IV and V), six normal modes in IR and six normal modes in Raman may be observed for each variant of the formate anion in the $Sc(HCOO)_3$ structure.

The observed IR vibrations (Table VI) correspond roughly to the generally accepted[7] fundamental vibration spectrum of the formate ion. However, similarly to formates of Sn(IV), Be(II), and Tl(I) (ref.[7]), the v_6 is very weak and probably overlaps the omnipresent NO_3^- anion (coming from the KBr carrier). No splitting is observed for the fundamental vibrations v_2, v_5, v_4. Splitting of the v_3 (observed also for strontium(II) formate[5]), and perhaps of v_1, could reflect differences between carbon––hydrogen bonds of the formate anions. To verify that, however, the solid state NMR spectrum would have to be recorded or structure refinement would have to be done from neutron data of a deuterated scandium formate.

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