$ScOH(CH_3SO_3)_2$, a Basic Methanesulfonate of Scandium with Chain Structure

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Single crystals of $ScOH(CH_3SO_3)_2$ were obtained from a solution of $Sc_2(CO_3)_3$ in methanesulfonic acid at pH 7. According to the X-ray single crystal structure determination, the compound crystallizes with the non-centrosymmetric orthorhombic space group $Pmc2_1$ ($Z = 8$, $a = 743.92(8)$, $b = 1497.7(3)$, $c = 1540.1(2)$ pm, $R_{all} = 0.0925$) and contains the Sc^{3+} ions in octahedral coordination of oxygen atoms which belong to two OH^- and four $CH_3SO_3^-$ ions. The linkage of the Sc^{3+} ions leads to chains according to the formulation $^1_\infty[Sc(CH_3SO_3)_{4/2}(OH)_{2/2}]$ which are oriented along the [100] direction and connected *via* hydrogen bonds. The IR spectrum of the compound shows the typical bands of the $CH_3SO_3^-$ ion.

Key words: Scandium, Methanesulfonate, Crystal Structure

Introduction

The crystal structures of lanthanide methanesulfonates are known for some trihydrates [1], dihydrates [2 – 4] and the anhydrous compounds of La, Nd, Er and Yb [1 – 3]. Except for the La case all of the anhydrous compounds crystallize with non-centrosymmetric crystal structures. They are potential candidates for non-linear optical properties. Furthermore, the thermal behaviour of the methanesulfonates is of special interest because it offers the possibility to synthesize oxide-disulfides, $M_2O_2S_2$, and oxide-sulfides, M_2O_2S, of the lanthanides at low temperatures [3, 5]. The syntheses of the methanesulfonates were generally carried out by the reaction of the lanthanide sesquioxides or carbonates with methanesulfonic acid. However, this procedure does not lead to a pure methanesulfonate in the case of scandium. Instead, the basic compound $ScOH(CH_3SO_3)_2$ is formed which is discussed in the present paper. The formation of basic salts occurs quite easily in solution of low acidity containing highly charged and small cations. For Sc^{3+} this has been shown for the halides $ScOHX_2{\cdot}6H_2O$ (X = Cl, Br) [6], the perchlorate $ScOH(ClO_4)_2{\cdot}H_2O$ [7] and for various basic sulfates, which are unfortunately not well characterized [8].

Experimental Section

Colorless single crystals of $ScOH(CH_3SO_3)_2$ were obtained by dissolving $Sc_2(CO_3)_3$ (Alfa, 99.9) in methanesulfonic acid (20% CH_3SO_3H, Fluka) until neutrality was achieved and evaporation of the solution in a desiccator for six weeks. Some of the needle shaped crystals were mounted in glass capillaries and their quality was checked by means of orientation images on a single crystal diffractometer (STOE IPDS I). From the best specimen reflection intensity data were collected using the same diffractometer. Inspection of the reflection conditions led to the space group $Pmc2_1$ (no. 26). Assuming this space group, structure solution and refinement with the help of the programs SHELXS86 and SHELXL93 [9, 10] were successful and yielded, after performing an absorption correction [11, 12], the data summarized in Tables 1 – 3. According to powder diffraction measurements (glass capillary, Debye-Scherrer geometry, STOE STADI P [13]) the product is not a pure phase but contains small amounts of another compound which has not been identified up to now. Some of the needle shaped crystals have been separated to measure an IR spectrum (KBr pellet, 400 – 4000 cm^{-1}, IFS66v/s, BRUKER).

Results and Discussion

$ScOH(CH_3SO_3)_2$ crystallizes with the non-centrosymmetric space group $Pmc2_1$. It contains two crys-

Table 1. Crystallographic data of $ScOH(CH_3SO_3)_2$.

Lattice parameters (single crystal/powder)	a = 743.92(8)/743.6(2) pm b = 1497.7(3)/1497.3(5) pm c = 1540.8(2)/1539.5(4) pm
Cell volume	1715.9(4)/1714.0(7) Å^3
No. of formula units	8
Crystal system	orthorhombic
Space group	$Pmc2_1$ (No. 26)
Diffractometer	Stoe IPDS-I
Radiation	Mo-K_α (graphite-monochrom., λ = 71.07 pm)
Temperature	20 °C
Data range	$5° < 2\theta < 54°$
Index range	$-8 \le h \le 9$ $-19 \le k \le 19$ $-20 \le l \le 20$
Rotation angle; φ-increment	$0° < \varphi < 200°$; 2.0°
No. of images	100
Exposure time	3 min
Detector distance	60 mm
Data corrections	polarization/Lorentz
Absorption correction	numerical [10, 11]
μ	13.4 cm^{-1}
No. of collected reflections	13020
No. of unique reflections	3399
No. of reflections with $I_o > 2\sigma(I)$	2046
R_{int}	0.0983
Structure solution and refinement	SHELXS-86 and SHELXL-93 [9, 10]
Scattering factors	Intern. Tables, Vol. C [16]
Goodness of fit	0.937
$R1$; $wR2$ $I_o > 2\sigma(I)$	0.0468; 0.0878
$R1$; $wR2$ (all data)	0.0925; 0.0966
Flack-x parameter	−0.02(7)
CCDC[a)]	224122

[a)] Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

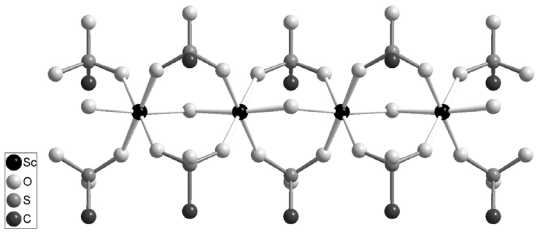

Fig. 1. $^1_\infty[Sc(CH_3SO_3)_{4/2}(OH)_{2/2}]$ chains in the crystal structure of $ScOH(CH_3SO_3)_2$. The Sc^{3+} ions are linked by two $CH_3SO_3^-$ groups and one OH^- ion. The chains are oriented in the [100] direction.

Table 2. Atomic positions and equivalent displacement parameters for $ScOH(CH_3SO_3)_2$.

Atom	Wyckoff site	x	y	z	[a)] $U_{eq} \cdot 10^{-1}$/ pm^2
Sc1	4*c*	0.7493(4)	0.50861(11)	0.01642(7)	19.3(3)
Sc2	4*c*	0.7496(3)	0.00352(10)	0.99484(7)	15.0(3)
O1	2*a*	0	0.9441(4)	0.9866(5)	17(2)
O2	2*b*	1/2	0.5615(5)	0.0509(5)	22(2)
O3	2*a*	0	0.4662(5)	0.9695(5)	26(2)
O4	2*b*	1/2	0.0644(4)	0.9938(5)	16(2)
S1	2*b*	1/2	0.8760(2)	0.8574(2)	21.1(7)
O11	2*b*	1/2	0.8853(7)	0.7645(5)	45(4)
O12	4*c*	0.6613(10)	0.9150(4)	0.8975(4)	32(2)
C1	2*b*	1/2	0.7607(10)	0.8856(10)	48(5)
S2	2*a*	0	0.1455(2)	0.8712(2)	21.0(7)
O21	2*a*	0	0.1478(7)	0.7772(5)	38(3)
O22	4*c*	0.8386(10)	0.1018(4)	0.9058(4)	29(2)
C2	2*a*	0	0.2550(8)	0.9145(11)	41(5)
S3	2*a*	0	0.6985(2)	0.0050(2)	20.2(7)
O31	2*a*	0	0.7657(5)	0.9382(6)	29(2)
O32	4*c*	0.8361(8)	0.6409(3)	0.0009(4)	28.7(14)
C3	2*a*	0	0.7495(8)	0.1067(8)	29(3)
S4	2*b*	1/2	0.3196(2)	0.0344(2)	24.2(7)
O41	2*b*	1/2	0.2536(5)	0.9649(6)	37(3)
O42	4*c*	0.3384(10)	0.3774(4)	0.0350(5)	42(2)
C4	2*b*	1/2	0.2642(9)	0.1328(9)	39(4)
S5	2*a*	0	0.1191(2)	0.1401(2)	22.8(8)
O51	2*a*	0	0.2158(7)	0.1424(9)	73(4)
O52	4*c*	0.1624(10)	0.0852(4)	0.0971(4)	34(2)
C5	2*a*	0	0.0740(16)	0.2448(10)	78(7)
S6	2*b*	1/2	0.1341(2)	0.6244(2)	21.2(8)
O61	2*b*	1/2	0.2295(6)	0.6139(7)	39(3)
O62	4*c*	0.6627(11)	0.0915(4)	0.5884(5)	40(2)
C6	2*b*	1/2	0.1058(11)	0.7328(9)	57(6)
S7	2*a*	0	0.5027(2)	0.2010(2)	21.7(7)
O71	2*a*	0	0.5682(7)	0.2680(5)	39(3)
O72	4*c*	0.1603(10)	0.5093(5)	0.1449(3)	43(2)
C7	2*a*	0	0.3959(10)	0.2452(11)	49(5)
S8	2*b*	1/2	0.4997(2)	0.8314(2)	23.4(7)
O81	2*b*	1/2	0.5697(7)	0.7677(6)	38(3)
O82	4*c*	0.6636(9)	0.5008(5)	0.8868(3)	37(2)
C8	2*b*	1/2	0.3943(9)	0.7802(9)	29(4)

[a)] $U_{eq} = 1/3[U_{11} + U_{22} + U_{33})]$ [17].

tallographically different Sc^{3+} ions which are located on general sites (4*c*) of this space group. The coordinates of the scandium ions (Table 2) suggest that they are symmetry related. In fact, the arrangement of the metal ions would allow higher symmetry, but for a proper description of the anions the space group symmetry must be reduced to $Pmc2_1$. Both of the Sc^{3+} ions are in octahedral coordination of oxygen atoms which belong to four monodentate $CH_3SO_3^-$ and two OH^- ions. The latter are in *trans* orientation with respect to each other with the respective angles O-Sc-O being 173 and 176°, respectively (Table 3). The distances

Table 3. Selected distances (pm) and angles (deg) for $ScOH(CH_3SO_3)_2$.

Sc1-O2		208.5(4)	Sc2-O4		206.8(3)
-O3		209.9(4)	-O1		206.8(4)
-O42		209.0(6)	-O52		209.9(6)
-O72		209.0(6)	-O12		210.6(6)
-O82		209.9(5)	-O22		211.7(6)
-O32		209.8(6)	-O62		212.6(6)
Sc1-Sc1		370.9(6)	Sc2-Sc2		371.3(4)
S1-O11		143.8(9)	S5-O51		144.9(10)
-O12	(2x)	147.1(7)	-O52	(2x)	146.8(7)
-C1		178.1(15)	-C5		175(2)
S2-O21		144.8(8)	S6-O61		143.9(9)
-O22	(2x)	146.8(7)	-O62	(2x)	147.6(7)
-C2		177.1(13)	-C6		172.3(14)
S3-O31		144.0(8)	S7-O71		142.4(9)
-O32	(2x)	149.4(6)	-O72	(2x)	147.6(6)
-C3		174.3(12)	-C7		173.9(14)
S4-O41		145.6(9)	S8-O81		143.7(10)
-O42	(2x)	148.2(7)	-O82	(2x)	148.6(6)
-C4		172.7(13)	-C8		176.4(12)
O2-Sc1-O3		173.2(3)	Sc2-O1-Sc2		128.5(3)
			Sc1-O2-Sc1		125.6(4)
O4-Sc2-O1		176.0(3)	Sc1-O3-Sc1		125.4(4)
			Sc2-O4-Sc2		127.7(3)
O11-S1-O12	(2x)	112.3(4)	O51–S5–O52	(2x)	110.9(4)
O12-S1-O12		109.4(6)	O52–S5–O52		110.8(5)
O11-S1-C1		109.7(7)	O51–S5–C5		111.3(10)
O12-S1-C1	(2x)	106.4(4)	O52–S5–C5	(2x)	106.3(5)
O21-S2-O22	(2x)	112.0(3)	O61–S6–O62	(2x)	112.8(4)
O22-S2-O22		109.8(5)	O62–S6–O62		110.1(6)
O21-S2-C2		110.7(7)	O61–S6–C6		110.7(7)
O22-S2-C2	(2x)	106.0(4)	O62–S6–C6	(2x)	105.0(4)
O31–S3–O32	(2x)	111.9(3)	O71–S7–O72	(2x)	112.2(4)
O32–S3–O32		109.3(4)	O72–S7–O72		107.7(5)
O31–S3–C3		109.7(6)	O71–S7–C7		110.5(7)
O32–S3–C3	(2x)	106.9(4)	O72–S7–C7	(2x)	106.9(5)
O41–S4–O42	(2x)	113.7(4)	O81–S8–O82	(2x)	112.6(3)
O42–S4–O42		108.4(5)	O82–S8–O82		109.9(5)
O41–S4–C4		108.6(6)	O81–S8–C8		110.4(6)
O42–S4–C4	(2x)	106.0(4)	O82–S8–C8	(2x)	105.5(4)
donor-acceptor distances for hydrogen bonds					
O1-O31		277.9	C1-O81		339.9
O2-O32	(2x)	287.3	C2-O71		347.8
O3-O82	(2x)	285.5	C3-O21		304.8
O4-O41		287.2	C4-O11		301.9
			C5-O21		337.7
			C6-O11		334.1
			C7-O51		313.1
			C8-O41		354.4

Sc^{3+}-O^{2-} lie between 207 and 213 pm with a significantly larger range for Sc(2) (Table 3). According to the formulation $^1_\infty[Sc(CH_3SO_3)_{4/2}(OH)_{2/2}]$ the anions link the Sc^{3+} ions to chains which are running along [100] (Fig. 1). The distances Sc^{3+}-Sc^{3+} in the chains

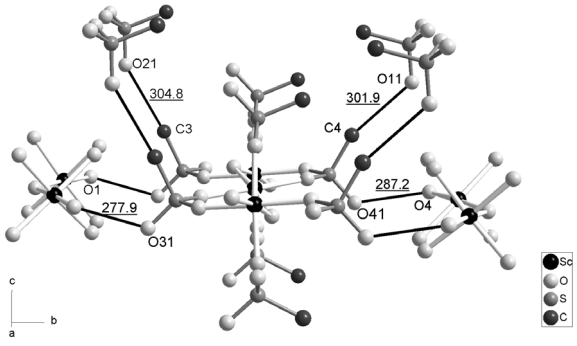

Fig. 2. Connection of the chains $^1_\infty[Sc(CH_3SO_3)_{4/2}(OH)_{2/2}]$ by hydrogen bonding (emphasized as black lines, distances in pm). In the [010] direction the hydrogen bonds have OH^- ions as donors while CH_3 groups act as donors in the [001] direction. In both cases non-coordinating oxygen atoms of the methanesulfonate ions are the acceptor atoms.

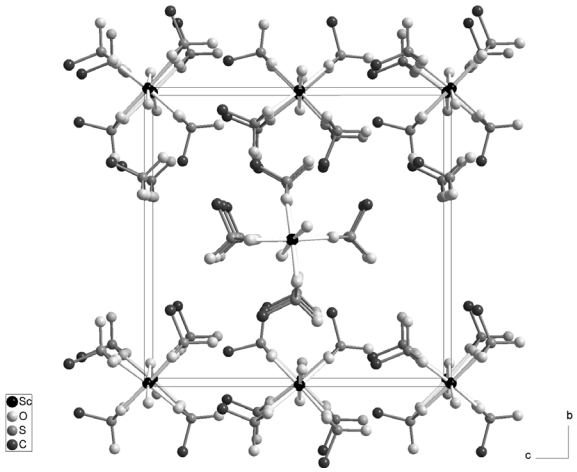

Fig. 3. Perspective view of the crystal structure of $ScOH(CH_3SO_3)_2$ along the [100] direction.

are 371 and 373 pm, respectively. Within the anions the distances S-C range from 173 to 178 pm while the average distances S-O are found to be 144.1 pm for the oxygen atoms which are not attached to Sc^{3+} ions and 147.8 pm for the coordinated ones. The observed angles at the sulfur atom do not differ very much from the ideal value for a tetrahedron (Table 3).

The connection of the chains is achieved by hydrogen bonding exclusively (Fig. 2). Although we were not able to locate the hydrogen atoms, the position of the hydrogen bonds could be estimated based on the respective donor-acceptor distances (Table 3). Judged from these values the hydrogen bonding system in-

Table 4. Assignment of the IR bands observed for $ScOH(CH_3SO_3)_2$.

assignment [15]	energy/cm^{-1}	vibration mode
	3430	ν(OH)
	3375	
ν_7	3033	ν_s(CH)
ν_1	2943	ν_{as}(CH)
ν_8	1417	$\delta_s(CH_3)$
ν_2	1338	$\delta_{as}(CH_3)$
ν_{10}	1259	ν_s(SO)
	1145	
	1110	
ν_4	1060	ν_{as}(SO)
ν_9	977	$\omega(CH_3)$
ν_3	788	ν(SC)
ν_5	551	$\delta_{as}(SO_3)$
ν_{11}	528	$\delta_s(SO_3)$
	476	

volves the OH^- ions as well as the CH_3 groups of the $CH_3SO_3^-$ anions as donors, while non-bonding oxygen atoms of the $CH_3SO_3^-$ groups act as acceptors. In the [010] direction the linkage of the chains occurs mainly *via* O-H-O bonds showing donor-acceptor distances of 278 (O1-O31) and 287 (O4-O41) pm. In the [001] direction only C-H-O hydrogen bonds are present with the C-O distances being 302 and 305 pm. These distances are very short with respect to the values discussed in the literature which range from 300 to 400 pm [14]. Further potential C-H-O hydrogen bonds are found with distances between 313 and 354 pm, and additional O-H-O bonds can be assumed from O2 to O32 and O3 to O82 (Table 3). The complete crystal structure is shown in Fig. 3.

The IR spectrum of $ScOH(CH_3SO_3)_2$ displays the typical vibrational bands of the methanesulfonate ion (Table 4) similar to those previously reported [15]. According to the literature, the bands between 1259 and 1060 cm^{-1} can be attributed to the S-O stretching vibrations, the S-C stretching mode is found at 788 cm^{-1}. The stretching vibrations of the CH_3 group are observed at 3033 (ν_{asym}(CH)) and 2943 cm^{-1} (ν_{sym}(CH)), respectively, the CH_3 deformation vibrations are located at 1417 and 1338 cm^{-1}. Furthermore, there is a rocking mode of the CH_3 group at 977 cm^{-1}. The SO_3 deformation vibrations are observed below 600 cm^{-1}. The O-H stretching vibrations are observed at 3375 and 3430 cm^{-1}. Table 4 summarizes the bands and their assignments.

Acknowledgments

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