DONOR–ACCEPTOR COMPLEXES OF SULFUR TRIOXIDE WITH 1,4-DIOXANE AND THEIR CRYSTAL STRUCTURES

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Dedicated to Professor Jaroslav Podlaha on the occasion of his 70th birthday.

Crystal and molecular structure of adducts $C_4H_8O_2{\cdot}SO_3$ and $C_4H_8O_2{\cdot}2SO_3$ were determined by X-ray structure analysis and Raman spectroscopy. Both compounds crystallize from excess of 1,4-dioxane as solvate $C_4H_8O_2{\cdot}SO_3{\cdot}C_4H_8O_2$, which was characterized by the same methods. Conditions for preparation of all the three compounds in high purity and good yields were optimized. Solvates $C_4H_8O_2{\cdot}H_2SO_4$ and $C_4H_8O_2{\cdot}H_2S_2O_7$ were identified among products of self-decomposition of $C_4H_8O_2{\cdot}SO_3$ and $C_4H_8O_2{\cdot}2SO_3$ in tetrachloromethane solution, respectively.

Keywords: Sulfur trioxide; 1,4-Dioxane; Donor–acceptor complexes; Crystal structure; Raman spectroscopy; X-ray diffraction; Crystal engineering.

The use of free sulfur trioxide as a sulfonation agent of organic compounds is limited due to its high reactivity and leads very often to charring. Therefore several attempts has been made to use less reactive donor–acceptor (D–A) complexes of the oxide for this purpose[1], the first of which was a use of rather non-reactive $py{\cdot}SO_3$ (refs[2–4]). The more reactive complexes of 1,4-dioxane, $C_4H_8O_2{\cdot}SO_3$ (**1**) and $C_4H_8O_2{\cdot}2SO_3$ (**2**), were used, e.g., in the sulfonation of olefins[5] and aromatic compounds[5,6]. Both complexes were prepared by the reaction of sulfur trioxide with 1,4-dioxane either in an inert solvent[5] or in the gas phase[7]. However, the pure complexes were not isolated and their crude mixture was used as a "D.S. Reagent"[5]. Until now, these complexes have not been obtained as pure compounds and their structure and bonding properties have not been studied. Calorimetric studies of the reaction of 1,4-dioxane with sulfur trioxide in 1,2-dichloroethane only confirmed their existence but excluded the existence of adducts with a

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higher content of sulfur trioxide, e.g. $C_4H_8O_2 \cdot 3SO_3$ (ref.[8]). Therefore we have attempted to find a suitable way of their isolation and to determine their molecular and crystal structures.

EXPERIMENTAL

Sulfur trioxide was obtained by distillation from 20% oleum (a solution of SO_3 in H_2SO_4), commercial 1,4-dioxane was purified and dried by common procedures. All operations were performed in Schlenk vessels under dry air.

Raman spectra (cm^{-1}) were recorded on a Raman module FRA 106/S connected with a Bruker IFS 55 Equinox spectrometer. The samples were measured directly in Schlenk vessels, the spectra were excited by the 1064 nm line of a Nd:YAG laser (350 mW). The line intensities are reported using a scale ranging from 0 to 10.

The X-ray intensity data were collected on a KUMA KM-4 CCD kappa-axis diffractometer using a graphite-monochromatized MoKα radiation (λ = 0.71069 Å). The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were inserted in calculated positions and isotropically refined assuming a “ride-on” model. Details of data collection and structure refinement are summarized in Table I. The program package SHELX97 (ref.[9]) was used for the structure determination and structure refinement, the drawings were made by the XP program of the Bruker SHELXTL V5.1 (ref.[10]) program package. CCDC 261233–261236 (**1**–**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Preparation of $C_4H_8O_2 \cdot SO_3$ (**1**)

Compound **2** (0.217 g, 0.874 mmol) was dissolved in nitromethane (10 cm^3) and 1,4-dioxane (0.074 cm^3, 0.874 mmol) was added under vigorous stirring. After 2–3 h standing at laboratory temperature the solvent was slowly distilled off under protective atmosphere and crystals of **1** (incongruent m.p. +52 °C) could be isolated in more than 95% yield.

Raman spectrum: 118 (1), 212 (8), 257 (2), 332 (2), 358 (1), 439 (1), 483 (2), 496 (3), 526 (2), 548 (3), 646 (2), 768 (3), 778 (4), 827 (1), 835 (1), 861 (2), 866 (3), 901 (1), 1002 (2), 1012 (2), 1046 (6), 1064 (9), 1126 (2), 1213 (3), 1255 (1), 1282 (1), 1302 (1), 1307 (2), 1313 (2), 1334 (1), 1341 (1), 1350 (2), 1375 (1), 1404 (1), 1446 (3), 1462 (2), 1472 (1), 2737 (1), 2792 (1), 2872 (3), 2884 (2), 2906 (2), 2923 (2), 2938 (3), 2974 sh (4), 2984 (10), 2998 (5), 3021 (2), 3042 (3), 3053 (3).

Preparation of $C_4H_8O_2 \cdot 2SO_3$ (**2**)

Tetrachloromethane (6 cm^3) was added to sulfur trioxide (0.306 g, 3.82 mmol) at –25 °C and under vigorous stirring a cool solution of 1,4-dioxane (0.163 cm^3, 1.91 mmol) in of tetrachloromethane (1 cm^3) was added. Immediately after adition of 1,4-dioxane solution, the fine white precipitate of **2** was formed. Well grown crystals acceptable for X-ray structure analysis can be obtained by recrystallization from nitromethane. Colorless crystals of **2** (incongruent m.p. +58 °C) could be isolated in 95% yield.

TABLE I
Crystal data and structure refinement

Parameter	**1**	**2**	**3**	**4**
Empirical formula	$C_4H_8O_5S$	$C_4H_8O_8S_2$	$C_8H_{16}O_7S$	$C_4H_{10}O_9S_2$
Formula weight	168.16	248.22	256.27	266.24
Temperature, K	120			
Wavelength, Å	0.71069			
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	P-1	P-1	$P2_1/n$	P-1
Unit cel dimensions, Å, °	a = 8.189(2) b = 8.863(2) c = 9.765(2) α = 90.61(3) β = 91.36(3) γ = 108.49(3)	a = 6.7010(10) b = 7.561(2) c = 8.729(2) α = 83.34(3) β = 80.20(3) γ = 89.93(3)	a = 9.1330(18) b = 9.3528(19) c = 10.649(2) α = 90 β = 98.96(3) γ = 90	a = 8.3120(17) b = 8.3477(17) c = 8.6031(17) α = 66.90(3) β = 61.80(3) γ = 80.31(3)
Volume, Å^3	671.8(3)	432.79(16)	898.5(3)	483.81(17)
Z	4	2	4	2
Calculated density, Mg m^{-3}	1.663	1.905	1.569	1.828
Absorption coefficient, mm^{-1}	0.444	0.635	0.358	0.582
F(000)	352	256	448	276
Crystal size, mm	0.20×0.08×0.08	0.15×0.05×0.05	0.15×0.1×0.05	0.10×0.10×0.02
θ range for data collection, °	3.17 to 28.41	2.71 to 28.22	3.50 to 28.49	3.27 to 28.25
Limiting indices	$-10 < h < 7$ $-11 < k < 11$ $-12 < l < 12$	$-8 < h < 8$ $-9 < k < 9$ $-11 < l < 9$	$-12 < h < 9$ $-12 < k < 12$ $-12 < l < 13$	$-10 < h < 9$ $-11 < k < 10$ $-11 < l < 6$
Reflections collected/unique	5253/2947 [R_{int} = 0.0354]	3287/1886 [R_{int} = 0.0677]	4898/2042 [R_{int} = 0.0497]	3562/2125 [R_{int} = 0.0366]
Completeness to 2θ = 25.00	97.3%	96.9%	98.6%	97.0%
Absorption correction	psi-scan	psi-scan	psi-scan	not measured
Max. and min. transmission	1.0000 and 0.7586	1.0000 and 0.6765	1.0000 and 0.6220	–
Refinement method	full-matrix least-squares on F^2			
Data/restrains/parameters	2947/0/181	1886/0/127	2042/0/118	2125/0/144
Goodness-of-fit on F^2	1.047	1.068	0.994	0.962
Final R indices [$I > 2\sigma$(I)]	R_1 = 0.0293 wR_2 = 0.0790	R_1 = 0.0456 wR_2 = 0.1166	R_1 = 0.0443 wR_2 = 0.0736	R_1 = 0.0315 wR_2 = 0.0690
R indices (all data)	R_1 = 0.0366 wR_2 = 0.0823	R_1 = 0.0528 wR_2 = 0.1194	R_1 = 0.0884 wR_2 = 0.0857	R_1 = 0.0501 wR_2 = 0.0729
Largest diff. peak and hole, e Å^{-3}	0.294 and –0.344	0.502 and –0.742	0.250 and –0.451	0.326 and –0.464

Raman spectrum: 135 (2), 144 (2), 189 (0), 297 (1), 331 (1), 441 (0), 477 (1), 515 (1), 534 (3), 550 (4), 780 (2), 785 (2), 828 (1), 834 (0), 1010 (1), 1025 (1), 1035 (0), 1069 (10), 1127 (1), 1214 sh (1), 1217 (1), 1296 (1), 1336 (1), 1343 (1), 1348 (1), 1358 (1), 1371 (1), 1407 (1), 1440 (3), 1458 (1), 1464 (0), 2749 (0), 2813 (0), 2867 (0), 2907 (0), 2968 (3), 2981 (4), 3028 (2), 3049 (2).

Preparation of $C_4H_8O_2{\cdot}SO_3{\cdot}C_4H_8O_2$ (**3**)

Two Schlenk vessels with SO_3 (1.1 g, 13.74 mmol) and 1,4-dioxane (10 cm^3, 117.36 mmol) were connected with a glass bent. The white solid substance formed on the wall of flask during 24 h was dissolved in 1,4-dioxane warmed to 45 °C. After cooling the colorless solution to laboratory temperature, well developed colorless crystals of **3** were obtained. The mother liquor was decanted and the rest of the solvent was evaporated under inert atmosphere at a low pressure. Crystals of **3** (incongruent m.p. +56 °C) could be isolated in 90% yield.

Raman spectrum: 206 (10), 252 (3), 335 (2), 353 (1), 436 (2), 480 (3), 493 (4), 531 (2), 550 (2), 644 (2), 773 (3), 833 (9), 853 (1), 867 (4), 1002 (1), 1015 (5), 1048 (6), 1065 (8), 1102 (1), 1127 (2), 1218 (3), 1278 (1), 1305 (5), 1336 (1), 1352 (1), 1370 (1), 1400 (1), 1442 (5), 1458 (2), 2664 (1), 2725 (1), 2786 (1), 2863 (6), 2891 (5), 2930 (4), 2963 sh (7), 2977 (10), 2983 (10), 3036 (2).

RESULTS AND DISCUSSION

The reaction of equimolar amounts of sulfur trioxide and 1,4-dioxane performed either in an inert solvent or in the gas phase always leads to a mixture of **1** and **2** which, when recrystallized from 1,4-dioxane, gives well developed crystals of solvate **3** only. When the reaction is carried out with SO_3 and 1,4-dioxane in molar ratio 2:1 in tetrachloromethane, pure microcrystalline **2** can be isolated. Crystals of **2** suitable for X-ray structure determination can be obtained by recrystallization from nitromethane. The most effective method of the preparation of **1** is the reaction of **2** with equimolar amounts of 1,4-dioxane in nitromethane. Recrystallization of both **1** and **2** from 1,4-dioxane leads always to the formation of **3**, as expected.

The solvent molecule of 1,4-dioxane in **3** can be removed at laboratory temperature in vacuo but this is always accompanied by partial decomposition of thus obtained **1** and, therefore, this procedure is not suitable for the preparation of pure **1**.

If the reaction mixtures of sulfur trioxide and 1,4-dioxane in molar ratios 1:1 and 2:1 in tetrachloromethane are kept at room temperature for several days, two dark-brown immiscible liquid layers are formed. Small amounts of the already known adduct $C_4H_8O_2{\cdot}H_2SO_4$ (ref.[11]) can be isolated at the ratio 1:1 by a careful vacuum reduction of the heavier layer. By a similar procedure, adduct $C_4H_8O_2{\cdot}H_2S_2O_7$ (**4**) can be obtained from a mixture with the 2:1 ratio of the reagents.

Description of Structures

Four molecules of **1** are included in general positions of the unit cell, one pair of those molecules forms dimer due to weak intermolecular S–O···S contacts (3.18 Å). These dimers are aligned in rows which are further arranged into layers. There are no intermolecular contacts between the other two molecules in unit cell, although the rows of these molecules form layers, surrounded by the layers built from dimers. The SO_3 groups of neighboring molecules in rows are oriented on opposite sides (Fig. 1).

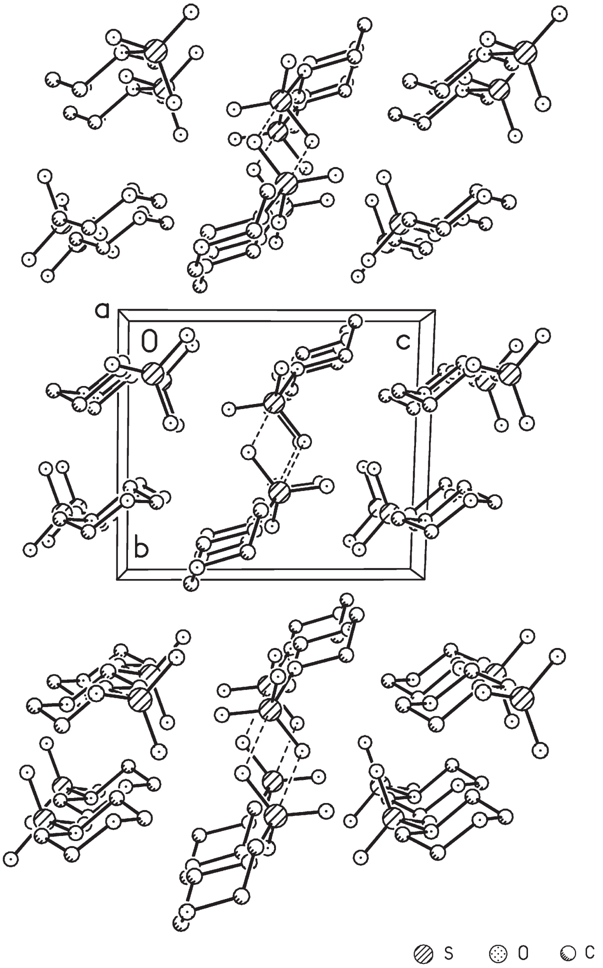

FIG. 1
Layers in structure **1** (hydrogen atoms are omitted for clarity)

The number of molecules in unit cell of **3** is identical to that of **1**, no intermolecular contacts can be observed. The layered structure of **1** is preserved also in **2** (Fig. 2). Orientation of SO_3 groups in neighboring layers is opposite. Between the double layers the layers of solvating 1,4-dioxane molecules lying in special centrosymmetric positions are inserted.

The unit cell of **2** depicted in Fig. 3 contains only two molecules lying in centers of symmetry. Molecules **2** are formed in rows and layers in a way similar to that in **1** and **3**. In the neighboring layers, the molecules are shifted forming the structural motive ABAB.

The average length of terminal S=O bonds in **1** and **2** is 1.422 Å identically, in **3** it is a little shorter (1.405 Å). Out of the studied adducts of sulfur trioxide and 1,4-dioxane, the D–A bond is the shortest (1.850 Å) in **2** and the longest (1.928 Å) in **3**, as was expected. The C–O bonds lengthening (0.05–0.06 Å) in bonded molecule of 1,4-dioxane as compared with the free molecule is due to the influence of D–A interaction. Changes in the C–C bond length are insignificant. The O=S=O angles in the O–SO_3 groups are the largest in **2** where the trigonal SO_3 pyramid is flattened.

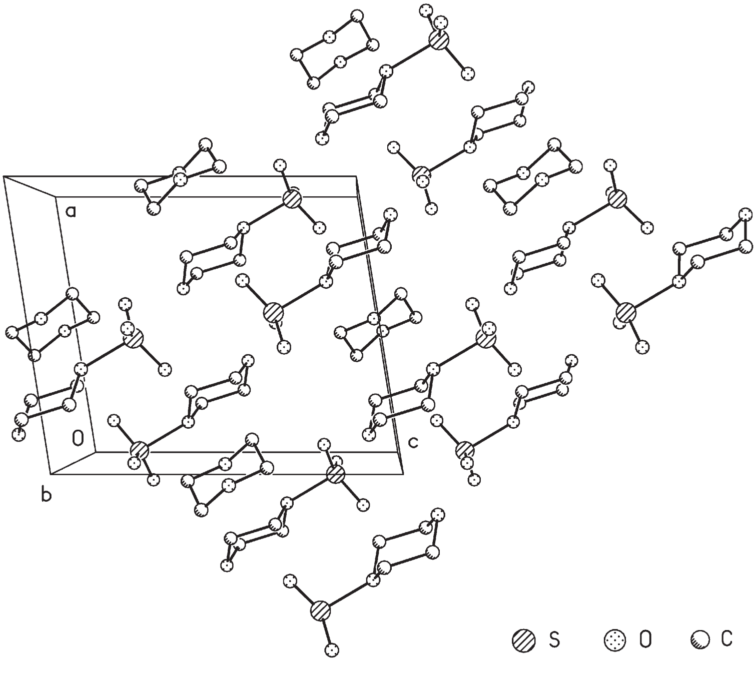

FIG. 2
Double layers in structure **3** (hydrogen atoms are omitted for clarity)

Due to relatively short (1.417 Å) hydrogen bonds in molecules **4** form collinear zigzag chains oriented in the direction of the unit cell diagonal [1 1 0] (Fig. 4). The molecules of $H_2S_2O_7$ are positioned on the top of chains and molecules of 1,4-dioxane join them. Pairs of $H_2S_2O_7$ molecules as well as 1,4-dioxane, are associated through symmetry centers, neighboring chains are shifted by a half of the elementary translation. There are no significant intermolecular interactions between chains.

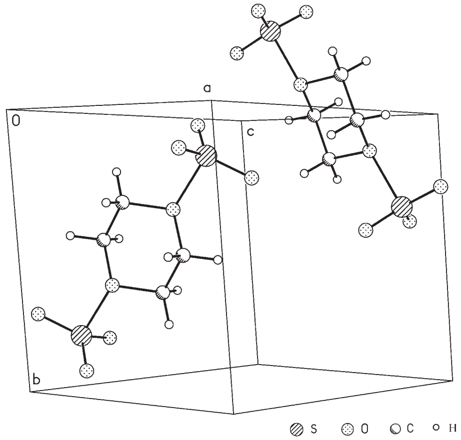

FIG. 3
Unit cell of **2**

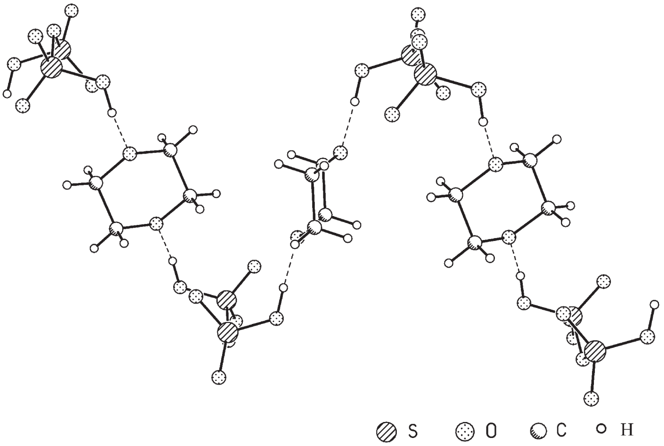

FIG. 4
Zigzag chain of **4**

Raman Spectra

Of compounds **1**, **2** and **3**, compound **2** shows the simplest Raman spectrum (Fig. 5) which is in full agreement with the centrosymmetry of its molecules (C_{2h}) – of a total of 60 normal vibrations only half of them are active in the Raman spectrum. The only absorption band which can be unequivocally identified in the spectrum is that of symmetrical valence vibration $\upsilon_s(SO_3)$ at 1069 cm^{-1}. Antisymmetric valence vibration bands of the SO_3 group can be expected in the region 1250–1350 cm^{-1} (e.g., 1298 and 1327 cm^{-1} in $Me_3N{\cdot}SO_3$ (ref.[12])) in which are also present deformation vibrations ω and τ of CH_2 groups of 1,4-dioxane molecules[13]. Bands at 770 and 785 cm^{-1} belong to fully symmetrical breathing vibrations of 1,4-dioxane rings. Due to D–A bonds the latter are shifted to lower frequencies as compared with those of free non-bonded 1,4-dioxane molecules (835 cm^{-1}). Deformation vibration bands of SO_3 groups lie in the region of 500–550 cm^{-1}, similarly to $Me_3N{\cdot}SO_3$ (567 and 543 cm^{-1}), in which valence vibrations of the S–O D–A bond are also situated (valence vibration of the S–N D–A bond in $Me_3N{\cdot}SO_3$ is at 618 cm^{-1}). Bands at 296 and 331 cm^{-1} belong to deformation vibrations $\rho(SO_3)$.

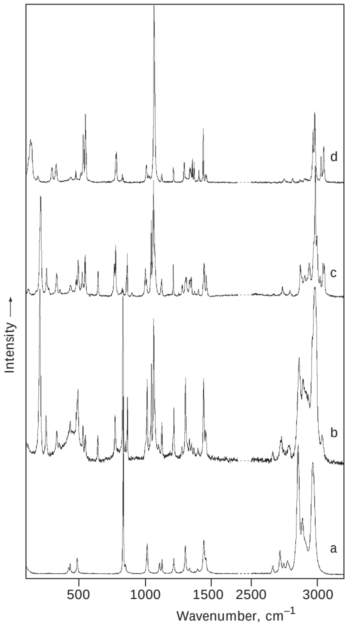

FIG. 5
Raman spectra of a 1,4-dioxane (a), and adducts **3** (b), **1** (c) and **2** (d)

The highest possible symmetry of the molecule **1** can be only C_s and, therefore, all 48 normal vibrations can be present in the Raman spectrum. However, the situation is complicated by the presence of two crystallographically non-equivalent molecules in the unit cell which fact can double the number of observed bands. This is suggested by splitting of the $\upsilon_s(SO_3)$ into a well-resolved doublet (1046 and 1064 cm^{-1}). Other $O–SO_3$ vibration bands can be interpreted in a similar way.

The character of the Raman spectrum of **3** is similar to that of **1**, as expected since the packing of the molecules in their crystal structures is closely related. The wavenumbers of bands belonging to solvate molecules of 1,4-dioxane are practically the same as those in free molecules (breathing vibration lies only 2 cm^{-1} lower) which complies with absence of intermolecular contacts in the crystal structure of **3**.

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