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Novel Cation $[N(SO_2NMe_3)_2]^+$ and Its Synthesis and Crystal Structure. Dichloride of Imido-bis(sulfuric) Acid $HN(SO_2Cl)_2$. Part 1. Crystal Structures of $KN(SO_2Cl)_2\cdot(1/2)CH_3CN$, $KN(SO_2Cl)_2\cdot(1/6)CH_2Cl_2$, and $[PCl_4][N(SO_2Cl)_2]$

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Several salts of bis(chlorosulfonyl)imide $HN(SO_2Cl)_2$ (**1**), namely, two solvates of its potassium salt, $KN(SO_2Cl)_2\cdot(1/2)CH_3CN$ (**1K1**), $KN(SO_2Cl)_2\cdot(1/6)CH_2Cl_2$ (**1K2**), and its tetrachlorophosphonium salt, $[PCl_4][N(SO_2Cl)_2]$ (**2**), were prepared and structurally characterized. The reaction of $HN(SO_2Cl)_2$ with Me_3N gives the $[N(SO_2Cl)_2]^-$ salt of a novel cation, $[N(SO_2NMe_3)_2]^+$. This cation is analogous to the $[HC(SO_2NMe_3)_2]^+$ cation, but in contrast to the latter, it is fairly stable to hydrolysis. The salt $[N(SO_2NMe_3)_2]^+[N(SO_2Cl)_2]^-$ (**3**) can be converted into salts of other anions by being treated with diluted aqueous solutions of the respective acids, and thus NO_3^-, $Cl^-\cdot H_2O$, SeO_3^{2-}, CH_3COO^-, HSO_4^-, $(COO)_2^{2-}$ salts were prepared. Treatment of **3** with concentrated HNO_3 gave the $[N(SO_2NMe_3)_2]^+[O_2NO{-}H{-}ONO_2]^-$ salt, and the addition of an HCl-acidified $FeCl_3$ aqueous solution yielded the $FeCl_4^-$ salt. Methanolysis resulted in the formation of $MeOSO_3^-$ and $[MeOSO_2NSO_2OMe]^-$ salts. All salts have been characterized by chemical analysis, vibrational spectroscopy, and X-ray structure determinations.

Introduction

In recent years, there has been an increased interest in the derivatives of imido-bis(sulfuric) acid (or sulfonylimides) and their salts (e.g., Li salts of bis(fluorosulfonyl)imide, bis(perfluoroalkoxy)sulfonylimide, and poly(perfluoroalkoxy)sulfonylimide). They appear to be promising compounds applicable as solutes in poly(ethylene oxide) electrolytes for lithium batteries,[1a−c] as treatments for viral infections (carbocyclic aminoderivatives),[1d] and as antiallergics (bis(aralkylamidosulfonyl)imides).[1e] Bis(perfluoroalkoxysulfonyl)imides and bis(dodecyloxysulfonyl)imide show a high surfactant activity,[1f,g] and metal salts of bis(trifluoromethylsulfonyl)imide are effective catalysts for Friedel−Crafts acylations.[1h,i] Moreover, bis(halogenosulfonyl)imides are also interesting from a theoretical point of view since they rank among the strongest neutral Brønsted acids.[2]

Because of the general interest and possible use of derivatives of imido-bis(sulfuric) acid, we performed both preparative and structural investigations of $HN(SO_2Cl)_2$ and its salts as a part of our systematic study of Cl_3PNSO_2Cl and its derivatives.

In this paper, we report structures of K^+ (**1K1** and **1K2**) and PCl_4^+ (**2**) salts of $HN(SO_2Cl)_2$ (**1**) and the synthesis and structure of a novel salt, $[N(SO_2NMe_3)_2]^+[N(SO_2Cl)_2]^-$ (**3**). We also present the synthesis and structures of some other salts of the $[N(SO_2NMe_3)_2]^+$ cation, namely, $[CH_3OSO_2NSO_2OCH_3]^-$ **(4)**, $CH_3OSO_3^-$ **(5)**, Cl^- **(6)**, NO_3^- **(7)**, $[O_2NO{-}H{-}ONO_2]^-$ (hereafter referred to as $[HN_2O_6]^-$) **(8)**, and $FeCl_4^-$ **(9)**. However, these salts were prepared and

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structurally characterized as a demonstration of the remarkable stability of the $[N(SO_2NMe_3)_2]^+$ cation. Therefore only selected relevant data are used in Table 3, and complete data were deposited.[28] Although the structure of **1** at −60 °C has already been published,[14] we have used our own determination at −123 °C for the purpose of comparison, but this will not be further discussed.

Results and Discussion

Salts of $HN(SO_2Cl)_2$. $HN(SO_2Cl)_2$ can be prepared by several routes, the most convenient being those of Cl_3PNSO_2Cl with HSO_3Cl[3] and $ClSO_2NCO$ with HSO_3Cl.[4] The strongly acidic proton of $HN(SO_2Cl)_2$ can be replaced by cations; several salts, such as the Ag^+, Li^+, Na^+, K^+, NO^+, NO_2^+, and PCl_4^+ [5−7] salts, have already been obtained, but to our knowledge, no structural characteristics of any of them have been given. According to Paul and Kapoor et al.,[8] treatment of **1** with Me_3N and Et_3N at low temperature or the reaction of **1** with Me_3NHCl or Et_3NHCl at room temperature gives appropriate ammonium salts. However, according to Appel and Helwerth,[9] the reaction of Me_3N with **1** at low-temperature yields a betaine $ClSO_2N^-SO_2N^{\oplus}Me_3$.

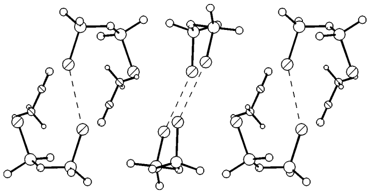

Figure 1. Anionic layer in **1K1**.

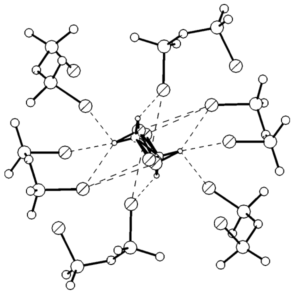

Figure 2. Arrangement of $N(SO_2Cl)_2$ anions around a disordered CH_2Cl_2 molecule in **1K2**.

It has been known for some time that sulfonyl chlorides $RNH-SO_2Cl$[10] and $R_1R_2CHSO_2Cl$[11,12] (R, R_1, R_2 = alkyl, aryl) react with tertiary amine bases to form base-stabilized imides, $RN^- = SO_2{\cdot}B^+$, and sulfenes, $R_1R_2C^- = SO_2{\cdot}B^+$, the zwitterion characters of which have been fully established by their X-ray structure determinations.[10,11] When the same reaction is performed with methanebis(sulfonyl chloride), $H_2C(SO_2Cl)_2$, a chloride salt of the zwitterion cation $[HC^-(SO_2N^+Me_3)_2]^+$ results.[13] Since there is a striking formal similarity between $H_2C(SO_2Cl)_2$ and $HN(SO_2Cl)_2$, we became interested in the nature of the betaine $ClSO_2N^-SO_2N^{\oplus}Me_3$.[9]

Depending on the solvent used for the crystallization of the K salt of $HN(SO_2Cl)_2$, we have obtained two solvates: $KN(SO_2Cl)_2{\cdot}(1/2)CH_3CN$ (**1K1**) and $KN(SO_2Cl)_2{\cdot}(1/6)CH_2Cl_2$ (**1K2**). While **1K1** exhibits a distinct layer structure, the structure of **1K2** may be described as a "column structure".

The crystal structure of **1K1** (Figure 1) is formed by alternating anionic and cationic layers parallel to the (100) plane. Each anionic layer is formed by two sublayers facing each other with their chlorines, with acetonitrile molecules between, and thus the anionic layers face the cations with their oxygens. There are apparent Cl···Cl contacts of 3.552 and 3.376 Å on the limits of the van der Waals radii (3.5 Å [15]) within the anionic layers. Both potassium cations are coordinated by 7 oxygen atoms (K(1), 2.746(3)−2.994(3) Å; K(2), 2.687(3)−3.096(3) Å) in a rather irregular arrangement.

In the crystal structure of **1K2** (Figure 2), there are six anions arranged with their chlorines around a disordered dichloromethane molecule in the form of a flat hexagonal disk, and the disks are stacked along the *a* axis into infinite, approximately hexagonal, columns. There are numerous Cl···Cl contacts among the anions and Cl atoms of dichloromethane, 3.348−3.550 Å, and the anion's chlorines and

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(28) Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. ICSD and CCDC 413093, 413094, 207960, 207961, 207962, 207968, 207967, 207964, 207963, 207966, and 207965 for **1**, **2**, **1K1**, **1K2**, **3**, **4**, **5**, **6**, **7**, **8**, and **9**, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Rd., Cambridge CB2 1EZ, UK.

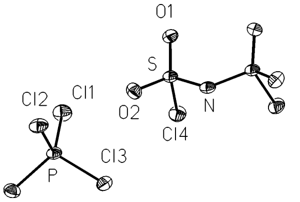
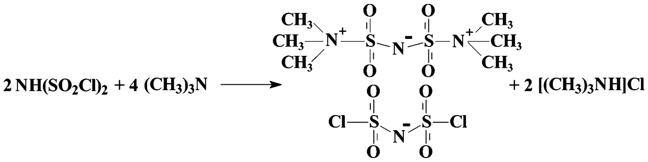


Figure 3. Molecular structure of the [PCl_4][N(SO_2Cl)$_2$]. Thermal ellipsoids are drawn with 50% probability.

Scheme 1. Chemical Reaction of Generation 3



dichloromethane hydrogens, 2.692−2.902 Å, but there is only one contact between anion's chlorines, 3.206 Å, within the disk and between the neighboring disks. For the sake of clarity, only theanion chlorines and dichloromethane hydrogen contacts are depicted in Figure 2. The cations are situated in the channels between adjacent columns and are coordinated by 8 oxygen atoms each (K(1), 2.645(3)−3.297(3) Å; K(2), 2.696(3)−3.346(3) Å; K(3), 2.670(3)−3.317(3) Å).

The structure of PCl_4^+[N(SO_2Cl)$_2$]$^-$ (**2**) (Figure 3) is formed by alternating cations and anions with only weak Cl···Cl interactions (3.554, 3.575 Å) between them. On the other hand, there are several Cl···O contacts (2.922−3.330 Å), shorter than or close to the limits of van der Waals radii (3.27 Å [15]) between the cations and anions.

Following the procedure described by Appel and Helwerth,[9] we have obtained, by the reaction of HN(SO_2Cl)$_2$ with Me_3N, a compound with a composition corresponding to the formula $ClSO_2N^-SO_2N^{\oplus}Me_3$. However, the study of the structure revealed that it is the salt [N(SO_2NMe_3)$_2$]$^+$-[N(SO_2Cl)$_2$]$^-$ (**3**) (Scheme 1). Contrary to HN(SO_2Cl)$_2$ and its K salts, which are extremely sensitive to water, this salt is fairly stable as witnessed by its synthesis, whereby the salt is precipitated by water from its acetonitrile solution. Particularly, the cation is a very stable species since **3** can be converted into salts of other anions by treatment with aqueous solutions of appropriate acids. Thus we have prepared NO_3^- (**6**) and $Cl^-{\cdot}H_2O$ (**7**) salts by the addition of solid **3** into a diluted (10−15%) solution of the appropriate acids. A similar treatment with an HCl-acidified $FeCl_3$ solution gave the $FeCl_4^-$ salt (**9**). If a rather concentrated (approximately 45%) solution of HNO_3 was used, the [N(SO_2NMe_3)$_2$]$^+$ salt of an uncommon hydrogen dinitrate anion [HN_2O_6]$^-$ (**8**) was isolated. However, our structure of this centrosymmetrical anion is in a full agreement with other reported data for this anion.[16−19] An addition of **3** into methanol yielded the [SO_3OCH_3]$^-$ salt (**5**), and a reaction of **3** with a solution of methanol in chloroform with cooling gave the [N(SO_3OCH_3)$_2$]$^-$ salt (**4**). The identities of all salts were confirmed by X-ray structure determinations.

It is apparent that the reaction of HN(SO_2Cl)$_2$ with Me_3N follows the same path as that of H_2C(SO_2Cl)$_2$, but there is a striking difference in the stability of the cations formed. While bis(trimethylaminesulfonyl)imidonium [N(SO_2NMe_3)$_2$]$^+$ cation is fairly stable toward water as already shown, the analogous bis(trimethylaminesulfonyl)-methanide [HC(SO_2NMe_3)$_2$]$^+$ cation, especially as the Cl^- salt, hydrolyzes readily.

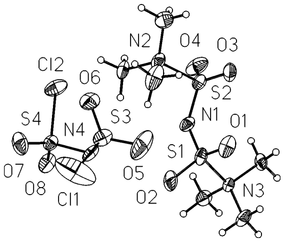


Figure 4. Molecular structure of the [N(SO_2NMe_3)$_2$]$^+$[N(SO_2Cl)$_2$]$^-$. Thermal ellipsoids are drawn with 50% probability.

Crystal structure of **3** (Figure 4) is formed by alternating cations and anions with no Cl···Cl or Cl···O contacts.

In this paper we present X-ray details for **2**, **1K1**, **1K2**, and **3** only (Table 1). A list of selected bond lengths and angles for **1**, **2**, **1K1**, **1K2**, and N(SO_2Cl)$^-$ anion of **3** is in Table 2. Table 3 shows selected interatomic angles and bond lengths for the [N(SO_2NMe_3)$_2$]$^+$ cation of **3**, **4**, **5**, **6**, **7**, **8**, and **9**.

−N(SO_2R)$_2$ Chain. As already noted,[20] the −N(SO_2R)$_2$ chain can have two geometrical forms. One with C_1 symmetry having both R substituents on the same side of the plane defined by S−N−S bonds (cis), and the other with C_2 symmetry (lower-energy form) with substituents on opposite sides of that plane (trans).[21,22] The actual geometry depends on the character of intermolecular or cation−anion interactions involving oxygen atoms of the −N(SO_2R)$_2$ chain. Thus, if there is only a simple system of hydrogen bonds (free imides), if the substituents, R (e.g., R = Cl, F, Me, Ph, etc.), cannot be involved in hydrogen bonding of their own, or if there are no −O···cation interactions, the preferred geometry is trans. This rule is fully reflected by actual structures of **1**, **1K1**, **1K2**, **2**, and **3**. While the geometries of the −N(SO_2R)$_2$ chains in HN(SO_2Cl)$_2$ **(1)** and [N(SO_2NMe_3)$_2$]$^+$[N(SO_2Cl)$_2$]$^-$ **(3)** are trans with the torsion angles, Cl−S···S−Cl, of 163.5 and 141.4°, respectively, since there is only a simple H-bond system in **1** and no −O···cation interaction in **3**, in the potassium **1K1** and **1K2** and PCl_4^+ **2** salts the anion has the cis arrangement because of numerous −O···cation interactions with torsion angles, Cl−S···S−Cl, of 20.5 and 36.0° in **1K1**, 22.0, 16.1, and 33.0 in **1K2**, and 0° in **2**.

As can be seen from Table 2, all S−N bond lengths are significantly shorter than that of the single S−N bond, 1.7714(3) Å, as found in HSO_3NH_2.[23] This bond shortening is more pronounced in deprotonized anions than in the HN(SO_2Cl)$_2$ molecule and can be attributed to a delocalization of nitrogen free-electron pairs along the S−N bonds. This fully explains the trigonal planar arrangement around the N atom in HN(SO_2Cl)$_2$, the sum of the angles being 360°. Cation−anion interactions influence not only the anion geometry but also the S−O bond lengths. It is apparent that the average S−O bond length is significantly longer in potassium salts which exhibit numerous K−O interactions

Table 1. Crystal Data and Structure Refinement of **2**, **1K1**, **1K2**, and **3**

	2	**1K1**	**1K2**	**3**
formula	$PCl_4^+[N(SO_2Cl)_2]^-$ $Cl_6NO_4PS_2$	$KN(SO_2Cl)_2$ $CH_{1.50}Cl_2KN_{1.50}O_4S_2$	$KN(SO_2Cl)_2$ $C_{0.17}H_{0.33}Cl_{2.33}KNO_4S_2$	$[N(SO_2NMe_3)_2]^+$ $[N(SO_2Cl)_2]^-C_6H_{18}Cl_2N_4O_8S_4$
fw	385.80	272.66	266.28	473.38
temp (K)	150	150	150	120
space group	*Pnma*	*C*2/*c*	*P*2$_1$/*n*	$P\bar{1}$
a (Å)	10.364(2)	22.256(4)	7.093(3)	6.6220(10)
b (Å)	10.679(2)	7.3300(10)	24.536(3)	12.330(2)
c (Å)	10.103(2)	22.285(4)	13.656(2)	13.010(3)
α (deg)	90	90	90	117.99(3)
β (deg)	90	107.41(3)	96.84(2)	98.04(3)
γ (deg)	90	90	90	94.14(3)
vol (Å)	1118.2(4)	3468.9(10)	2359.7(11)	917.2(3)
Z	4	16	12	2
D (Mg/m^3)	2.292	2.088	2.249	1.714
R indices [$I > 2\sigma(I)$]	R1 = 0.0617[a]	R1 = 0.0308[a]	R1 = 0.0343[a]	R1 = 0.0409[a]
R indices (all data)	R1 = 0.0637	R1 = 0.0863	R1 = 0.0518	R1 = 0.0871

[a] $R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[N(SO_2Cl)_2]^-$ Anion

	1[c]	**2**	**1K1**	**1K2**	**3**[b]
S−Cl	1.985(1) 1.982(1)	2.044(2)	2.034(1) 2.027(1) 2.033(1) 2.023(1)	2.009(1) 2.034(1) 2.027(1) 2.030(1) 2.027(1) 2.017(1)	2.028(5) 2.035(4)
S−O[a]	1.414(2)	1.418(4)	1.426(1)	1.426(1)	1.412(1)
S−N	1.646(2) 1.630(2)	1.574(3)	1.575(3) 1.574(3) 1.575(3) 1.583(3)	1.588(3) 1.569(3) 1.574(3) 1.577(3) 1.580(3) 1.580(3)	1.560(10) 1.580(9)
P−Cl		1.917(2) 1.923(2) 1.932(3)			
S−N−S	125.7(1)	122.8(4)	123.2(2) 122.5(2)	123.4(2) 124.1(2) 121.2(2)	121.3(6)
−O···H−	2.163(2) 2.342(2)				

[a] Average values; errors are esd's of the averages. [b] Anion only. [c] Our results.

than it is in the free imide with only weak hydrogen bonds and in salts **2** and **3** with no cation−anion interactions.

$[N(SO_2NMe_3)_2]^+$ Cation. The $[N(SO_2NMe_3)_2]^+$ cation can be regarded as a base-stabilized $[N(SO_2)_2]^+$ cation with S−N(3)Me$_3$ and S(2)−N(2)Me$_3$ donor−acceptor bonds as evidenced by a significant extension of the S−NMe$_3$ bond lengths (av value = 1.822 Å) as compared to S−N single bond, 1.7714(3) Å, found in HSO_3NH_2.[23] A similar extension of S−N bonds was observed in Me_3N-SO_3 [24] (S−N = 1.844(2) Å) and Me_2HN-SO_3 [25] (mean S−N = 1.790(6) Å), which was attributed to the bulkiness of methyl groups.[24] However, the problem might be more complex since this extension of the S−N bond is accompanied by a change of the S−O bond lengths (Table 4). However, the N(1)−S(1) and N(1)−S(2) bond lengths (av. value = 1.568 Å) (Table 3, Figure 4) are comparable with those found in the $[N(SO_2Cl)_2]^-$ anion (av. value = 1.576 Å).

Experimental Section

Synthesis. $KN(SO_2Cl)_2$. Dry KCl (12.7 g, 170 mmol) was added to a solution of 30 g (140 mmol) of $HN(SO_2Cl)_2$ dissolved in 30 mL of acetonitrile. The reaction mixture was slowly warmed to 60−70 °C and kept at this temperature overnight. A dark-brown, thick solution thus formed; it solidified upon cooling to the ambient temperature. The raw product was purified by dissolving it in a minimum amount of acetonitrile, filtered to remove unreacted KCl, and precipitated with CH_2Cl_2. The purified salt was filtered off and dried in vacuo for at least 30 min to obtain unsolvated salt. Yield: 27.7 g (78.5%). Anal. Calcd for **1K2**: S, 24.08; N, 5.26; Cl, 31.06. Found: S, 24.90; N, 5.87; Cl, 31.43. Deviations are the result of the presence of a lean compact solvate of CH_2Cl_2. Raman spectra (relative intensity) of $KN(SO_2Cl)_2$: 176 (22), 200 (37), 301 (25), 317 (33), 340 (23), 392 (15), 404 (100), 432 (47), 528 (18), 560 (10), 604 (10), 645 (51), 769 (19), 1057 (15), 1124 (13), 1181 (13), 1193 (49), 1322 (20), 1331 cm^{-1} (27%). Crystals suitable for X-ray measurements were obtained either by slow diffusion of benzene vapors into an acetonitrile solution in a closed container (**1K1**) or by direct crystallization from CH_2Cl_2 (**1K2**).

$KN(SO_2Cl)_2$ is extremely soluble in polar solvents such as acetonitrile or nitromethane, mildly soluble in dichlormethane, and almost insoluble in hexane or benzene.

$PCl_4^+[N(SO_2Cl)_2]^-$ (2). The salt was prepared according to the procedure given by Ruff.[6] A slurry of 12.0 g (57.6 mmol) of PCl_5 in 10 mL of $POCl_3$ was slowly added to 12.35 g (57.7 mmol) of $HN(SO_2Cl)_2$ dissolved in 10 mL of CCl_4 in a 50 mL Schlenk vessel at room temperature, and the mixture was refluxed for 1 h. When cooled to 10 °C, the product crystallized out. The crystals were removed by filtration in an inert atmosphere to give 18.22 g (82.0%) of **2**. Anal. Calcd for **2**: S, 16.62; N, 3.63; Cl, 55.13; P, 8.03. Found: S, 16.97; N, 3.75; Cl, 50.82; P, 8.54. The ^{31}P NMR spectra of a $CHCl_3$ solution of **2** shows a singlet of chemical shift 89.6 ppm appertain to PCl_4^+ group. Raman spectra (relative intensity) of **2**: 126 (10), 176 (33), 183 (32), 190 (30), 250 (45), 295 (19), 311 (25), 340 (17), 388 (100), 408 (28), 457 (84), 459 (60), 524 (10), 541 (10), 574 (25), 610 (10), 644 (12), 662 (19), 746 (10), 759 (10), 1177 (35), 1332 (10), 1343 (10), 1355 cm^{-1} (15%).

$[N(SO_2NMe_3)_2]^+[N(SO_2Cl)_2]^-$ (3). The salt was prepared by a modified procedure of Appel and Helwerth.[9] A 5.9 g (100 mmol) sample of Me_3N dissolved in 400 mL of CH_3CN was very slowly added, with stirring, to a solution of 10.5 g (50 mmol) $HN(SO_2Cl)_2$ in 300 mL of CH_3CN cooled to −40 °C. When a white

Table 3. Bond Lengths (Å) and Angles (deg) for [N(SO$_2$NMe)$_2$]$^+$ Cation

	3	**4**	**5**[a]	**6**[a]	**7**	**8**	**9**
N(1)−S(1)	1.575(1)	1.570(2)	1.570(3)	1.566(6)	1.576(1)	1.572(2)	1.550(10)
N(1)−S(2)	1.541(9)	1.569(2)	1.573(3)	1.552(6)	1.574(2)	1.567(2)	1.599(10)
S(1)−O(1)	1.405(8)	1.422(2)	1.426(2)	1.415(6)	1.420(1)	1.416(2)	1.365(12)
S(1)−O(2)	1.407(8)	1.422(2)	1.424(2)	1.405(2)	1.418(1)	1.419(2)	1.402(11)
S(2)−O(3)	1.411(8)	1.422(2)	1.423(1)	1.420(3)	1.419(1)	1.425(2)	1.394(9)
S(2)−O(4)	1.400(9)	1.415(2)	1.423(2)	1.410(3)	1.419(1)	1.414(2)	1.406(8)
S(1)−N(3)	1.822(8)	1.825(2)	1.829(1)	1.808(5)	1.817(1)	1.820(2)	1.826(7)
S(2)−N(2)	1.822(9)	1.816(2)	1.826(2)	1.811(3)	1.824(1)	1.822(2)	1.836(7)
S(1)−N(1)−S(2)	126.8(6)	127.5(1)	127.5(4)	126.3(7)	125.1(1)	126.3(2)	126.4(6)
N(1)−S(1)−N(3)	99.7(4)	103.0(1)	103.8(4)	101.4(8)	102.5(1)	103.2(1)	102.9(4)
N(1)−S(2)−N(2)	100.8(5)	102.6(1)	103.6(2)	101.4(8)	102.5(1)	103.6(1)	103.0(4)
O(1)−S(1)−O(2)	120.5(5)	119.8(1)	119.8(2)	119.8(3)	119.6(1)	119.9(1)	123.8(12)
O(3)−S(2)−S(4)	119.9(6)	119.7(1)	120.1(3)	120.1(4)	119.7(1)	119.3(1)	121.7(6)

[a] Average values; esd's are errors of the averages.

Table 4. Comparison of Average S−N, S−O, and N−C Bond Lengths (Å)

	[N(SO$_2$NMe$_3$)$_2$]$^+$	Me$_3$NSO$_3$[24]	Me$_2$HNSO$_3$[25]	H$_3$NSO$_3$[23]
S−N	1.822(7)[a]	1.844(2)	1.790(6)	1.7714(3)
S−O	1.449(8)[a]	1.405(2)	1.430(5)	1.442(3)
N−C	1.496(6)[a]	1.496(2)	1.504(10)	

[a] Average values from **3**, **4**, **5**, **6**, **7**, **8**, and **9**; errors are esd's of the averages.

precipitate of [Me$_3$NH]Cl began to form in the solution, the addition of Me$_3$N was stoppeded, and the reaction mixture was warmed to ambient temperature and stirred for 30 min. Then the addition of the Me$_3$N solution was continued until all of it was consumed. The mixture was then stirred for another 30 min; precipitated [Me$_3$NH]Cl was filtered off, and the volume of the solution was reduced to 1/10 in vacuo. The salt was then precipitated by the addition of a 10-fold excess of a water−ice mixture under intense stirring; it was filtered off on a sintered glass filter, washed with ethanol, and dried in vacuo to give 5.68 g (48%) of **3**. Anal. Calcd for **3**: S, 27.09; N, 11.84; Cl, 14.98. Found: S, 27.20; N, 11.41; Cl, 14.29. The ^{1}H NMR spectrum of a CH$_3$CN solution of **3** shows a singlet chemical shift of 3.6 ppm attributed to the N(CH$_3$)$_3$ group. The ^{13}C{^{1}H} NMR spectrum shows a singlet of chemical shift of 41 ppm. Raman spectra (relative intensity) of **3**: 161 (28), 178 (45), 208 (20), 291 (19), 305 (21), 326 (50), 382 (100), 412 (45), 435 (10), 464 (15), 524 (15), 533 (14), 574 (40), 589 (18), 624 (10), 638 (10), 764 (18), 783 (37), 967 (15), 1058 (10), 1110 (10), 1153 (10), 1192 (80), 1362 (15), 1411 (10), 1447 (17), 1462 (18), 2806 (10), 2859 (10), 2878 (10), 2920 (45), 2958 (25), 3030 (38), 3044 (20), 3052 cm^{-1} (18%). The raw salt was purified by precipitation from its saturated acetonitrile solution by addition of a 5-fold excess of ethanol cooled to −40 °C. Crystals suitable for X-ray measurements were obtained by crystallization from CH$_3$CN.

[N(SO$_2$NMe$_3$)$_2$]$^+$[MeOSO$_2$NSO$_2$OMe]$^-$ (4) and [N(SO$_2$NMe$_3$)$_2$]$^+$MeOSO$_3$$^-$ (5). Salts **4** and **5** were prepared from **3** by solvolysis in methanol solution. Salt **4** was prepared by low-temperature solvolysis in excess of dry MeOH; 2.2 g (5.7 mmol) of solid **3** was added to 10 mL of dry MeOH with stirring. The reaction mixture was kept at 0 °C, and the slurry very slowly dissolved. Then the mixture was stirred for another 30 min. After that, the volume of the solution was reduced to 1/10 in vacuo. The salt was then crystallized, filtered off on a sintered glass filter, washed with 2 mL of cool MeOH (−10 °C), and dried in vacuo to give 1.6 g (73%) of **4**. Anal. Calcd for **4**: S, 29.65; N, 12.96. Found: S, 29.48; N, 13.11. The ^{1}H NMR spectrum of a CHCl$_3$ solution of **4** shows two singlet chemical shifts of 3.6 and 3.75 ppm, attributed to N(CH$_3$)$_3$ and OCH$_3$ groups. The ^{13}C{^{1}H} NMR spectrum shows two singlets with chemical shifts of 41 and 48 ppm. The raw salt was purified by recrystallization from its saturated methanol solution under very slow cooling to −20 °C, forming crystals suitable for X-ray measurements.

Salt **5** was prepared by solvolysis at elevated temperature in an excess of dry MeOH; 1.1 g (4.3 mmol) of solid **3** was added to a 10 mL of dry MeOH with stirring. The reaction mixture was kept at 65 °C until the slurry dissolved. Then the mixture was stirred for another 30 min. After that, the volume of the solution was reduced to 1/10 in vacuo. The salt was then crystallized, filtered off on a sintered glass filter, washed with 2 mL of cool MeOH (−10 °C), and dried in vacuo to give 1.1 g (88%) of **5**. Anal. Calcd for **5**: S, 25.89; N, 11.32. Found: S, 25.70; N, 11.56. The ^{1}H NMR spectra of a CH$_3$OH solution of **5** shows two singlets with chemical shifts of 3.6 and 3.48 ppm attributed to N(CH$_3$)$_3$ and OCH$_3$ groups. The ^{13}C{^{1}H} NMR spectra show two singlets with chemical shifts of 41 and 53 ppm. The raw salt was purified by recrystallization of a saturated methanol solution under very slow cooling to −20 °C to obtain crystals suitable for X-ray measurements.

Other Salts Containing the [N(SO$_2$NMe$_3$)$_2$]$^+$ Cation (6, 7, 8, and 9). Other salts of the [N(SO$_2$NMe$_3$)$_2$]$^+$ cation were prepared from **3** by reacting it with an excess of a diluted (10−15%) aqueous solution of the corresponding acid. Salts **6** (Cl$^-$) and **7** (NO$_3$$^-$) were prepared from **3** by anion exchange reaction in aqueous solution of mineral acids (HNO$_3$ and HCl); 1 g (2.5 mmol) of solid **3** was added to a 10 mL aqueous solution of HNO$_3$ or HCl with stirring. The reaction mixture was warmed to 70 °C to dissolve the slurry. Then the mixture was stirred for another 10 min. After that, the reaction mixture was cooled to ambient temperature. The salt was then crystallized, filtered off on a sintered glass filter, washed with 2 mL of cool ethanol (−10 °C), and dried in vacuo to give approximately 0.3−0.5 g (55−90%) of **6** and **7**. Anal. Calcd for **6**: S, 20.43; N, 13.39; Cl, 11.30. Found: S, 20.97; N, 13.74; Cl, 11.60. The ^{1}H NMR spectrum of an aqueous solution of **6** shows a singlet at 3.6 ppm, attributed to the N(CH$_3$)$_3$ groups. The ^{13}C{^{1}H} NMR spectrum shows a singlet at 41 ppm. Anal. Calcd for **7**: S, 19.89; N(ammonium), 13.04%; $\sum$ N, 17.38. Found: S, 20.18; N(ammonium), 12.86; $\sum$ N, 16.91. The ^{1}H NMR spectrum of an aqueous solution of **7** shows a singlet at 3.6 ppm, attributed to the N(CH$_3$)$_3$ groups. The ^{13}C{^{1}H} NMR spectrum shows a singlet at 41 ppm. Raman spectra (relative intensity) of **3**: 175 (22), 257 (10), 297 (10), 336 (25), 364 (10), 389 (10), 396 (10), 431 (10), 459 (10), 476 (12), 524 (23), 548 (10), 598 (22), 630 (20), 708 (10), 763 (10), 777 (29), 944 (10), 960 (10), 1047 (100), 1116 (10), 1197 (40), 1364 (10), 1383 (10), 1408 (10), 1446 (13), 1477 (13), 1488 (14), 2806 (10), 2865 (12), 2902 (12), 2965 (22), 2982 (23), 3037 (28), 3054 cm^{-1} (20%). The raw salt was purified by recrystallization from its saturated methanol solution by cooling it very slowly to −20 °C, and crystals suitable for X-ray measurements were thus obtained.

When rather concentrated (45%) HNO_3 was used for the reaction of **3**, we isolated hydrogen dinitrate $[HN_2O_6]^-$ (**8**). Anal. Calcd for **8**: S, 16.64; N(ammonium), 10.90; $\sum$ N, 18.18. Found: S, 16.03; N(ammonium), 10.07; $\sum$ N, 20.45. Deviations are the result of the presence of free nitric acid (reaction-mixture solution on the crystal surface). The ^1H NMR spectrum of an aqueous solution of **8** shows two singlets at 3.5 and 13.2 ppm, attributed to the $N(CH_3)_3$ groups and HNO_3, respectively. The $^{13}C\{^1H\}$ NMR spectrum shows a singlet of chemical shift 41 ppm.

A similar treatment of **3** with HCl-acidified $FeCl_3$ solution gave the $FeCl_4^-$ salt **9**. The reaction procedure was the same as that used in the preparation of **6**, **7**, and **8**. Anal. Calcd for **9**: S, 14.00; N, 9.18; Cl, 30.96. Found: S, 14.13; N, 9.33; Cl, 30.70. The ^1H NMR spectrum of an aqueous solution of **9** shows a singlet at 3.6 ppm, attributed to the $N(CH_3)_3$ groups. The $^{13}C\{^1H\}$ NMR spectrum shows a singlet at 41 ppm.

X-ray Structure Analysis. The intensity data were collected on a KUMA KM-4 κ-axis diffractometer using a graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) equipped with an Oxford Cryosystem LT device at 120 K and corrected for absorption effects using ψ-scan methods. 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. The crystal data for compounds **1**, **2 1K1**, **1K2**, and **3** and other relevant information are summarized in Table 1, and a list of selected interatomic distances and angles is in Table 2. Table 3 lists important bond lengths and angles for the $[N(SO_2NMe)_2]^+$ cation.

The SHELX-97[26] program package was used for the structure determination and structure refinement and for the tables, and the drawings were made using the XP program of Bruker SHELXTL version 5.1.[27]

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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