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The $(SO_2)_2N_3^-$ Anion

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The recently proposed $(SO_2)_2N_3^-$ anion was structurally characterized by single-crystal X-ray diffraction of the $[Cs][(SO_2)_2N_3]$ salt ($P2_1/c$, $a = 8.945(2)$ Å, $b = 10.454(2)$ Å, $c = 8.152(2)$ Å, $\beta = 109.166(3)°$, $Z = 4$, and $R_1 = 0.0329$ at 130 K). In the $(SO_2)_2N_3^-$ anion, both SO_2 ligands are coordinated to one terminal nitrogen atom of the N_3^- anion.

Introduction

Sulfur dioxide has been extensively used as a nonaqueous inorganic solvent,[1–3] and many SO_2 solvates of metal cations have been structurally well characterized by X-ray crystallography.[4] Halide and pseudo-halide anions, such as F^-,[5,6] Cl^-,[6,7] Br^-,[6] I^-,[6,8] CN^-,[9] SCN^-,[10] OCN^-,[11] and recently N_3^-,[11,12] were also found to form adducts with SO_2 in a 1:1 ratio. These adducts can be viewed as halosulfites and pseudo-halosulfites. The strength of the bond between these anions and SO_2 was found to decrease with increasing anion size.[6,11,13] In the SO_2F^- anion, for example, the S−F bond is basically a single bond, while the S-anion bonds in SO_2I^- and SO_2SCN^- are best described as contacts or secondary bonds.[5]

In a recent paper in this journal, we reported the syntheses and characterization of the $[M][SO_2N_3]$ and $[M][(SO_2)_2N_3]$ salts, where M was $N(CH_3)_4$ and Cs.[12] These salts are of significant interest for polynitrogen chemistry because SO_2 is an excellent solvent for carrying out metathetical reactions involving azide ions. Because the reactions of the azide ions with the SO_2 solvent can complicate the desired metathetical reactions, a better understanding of the nature of these $(SO_2)_nN_3^-$ adducts is very important. Whereas the $[M][SO_2N_3]$ salts were well characterized by single-crystal X-ray diffraction, the $[M][(SO_2)_2N_3]$ salts were characterized only by vibrational spectroscopy. Although the vibrational spectra favored a structure in which both SO_2 molecules are attached to the same terminal nitrogen atom of the azide ion, a more definite proof for the proposed structure was highly desirable. There were two previous reports on adducts with an SO_2 to anion ratio of larger than 1, but none provided any structural evidence. Thus, in 1938, Jander and Mesech have studied the interaction of SO_2 with the halide and SCN^- anions by vapor pressure measurements. They found evidence for the existence of 1:2, 2:1, 3:1, and 4:1 adducts, depending on the nature of the anion and countercation.[14] Similarly, a UV and infrared spectroscopic study of halides and halosulfites

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in SO_2 solution provided evidence for the presence of 2:1 adducts; however, questionable structures were proposed for these $(SO_2)_2X^-$ anions that involved an $O_2S{-}SO_2$ moiety, coordinated to the halides through only one sulfur atom.[6]

In the present paper, we report the X-ray crystal structure of $[Cs][(SO_2)_2N_3]$, thereby establishing the structure of the $(SO_2)_2N_3^-$ anion beyond doubt.

Experimental Section

Caution! *Azides are highly endothermic and often can decompose explosively. Although no explosion has occurred while conducting these experiments, the materials should be handled on a small scale with appropriate safety precautions.*

Materials and Apparatus. Reactions were carried out in Teflon-FEP ampules that were closed by stainless steel valves. Volatile materials were handled on a Pyrex glass vacuum line equipped with grease-free Kontes glass−Teflon valves. Nonvolatile solids were handled in the dry argon atmosphere of a glovebox. The CsN_3 was prepared by literature methods.[15] The SO_2 (Air Products, anhydrous grade, 99.9%) was dried over CaH_2.

Crystal Growth of $[Cs][(SO_2)_2N_3]$. Inside the drybox, approximately 0.02 g of CsN_3 (0.07 mmol) was loaded into a 9-mm FEP tube, which was sealed on one side and fused to a piece of 3/8 in. FEP tubing equipped with a Whitey SS−IRF2 valve on the other side. Anhydrous SO_2 (0.5 mL) was added in vacuo to the solid at −196 °C. After warming to room temperature to dissolve all the CsN_3, the tube was cooled to −64 °C, and the SO_2 solvent was removed slowly under a dynamic vacuum at −64 °C, yielding a pale yellow crystalline solid. The ampule was cut open at −78 °C under a dry nitrogen stream, and the crystals were immediately transferred into an aluminum trough, kept at −100 °C by a stream of cold dry nitrogen. A crystal selected in the cold stream was mounted on a glass fiber by rapidly bringing it into contact with a droplet of Fomblin oil (Z-25) adhering to the tip of the fiber. The mounted crystal was rapidly transferred into the cold nitrogen stream of the goniometer head. The crystal used in this study had the dimensions $0.80 \times 0.34 \times 0.313$ mm^3.

Crystal Structure Determination of $[Cs][(SO_2)_2N_3]$. (a) Collection and Reduction of X-ray Data. X-ray diffraction data were collected using a Bruker 3-circle platform diffractometer, equipped with a SMART APEX CCD (charge coupled device) detector with the χ-axis fixed at 54.74° (using the program SMART[16]), and using Mo Kα radiation ($\lambda = 0.71073$ Å) from a fine-focus tube. The diffractometer was equipped with a cryo-cooler from CRYO Industries for low-temperature data collection using controlled liquid nitrogen boil off. Cell constants were determined from 60 10-s frames at 130 K. A complete hemisphere of data was collected up to a resolution of 0.75 Å. Processing was carried out by using the program SAINT,[17] which applied Lorentz and polarization correction to three-dimensionally integrated diffraction spots. The program SADABS[18] was used for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections.

(b) Solution and Refinement of the Structure. All data were processed using the SHELXTL package (version 5.1)[19] for structure determination, refinement, and molecular graphics. The XPREP program was used to confirm the unit cell dimensions and the crystal lattices. The structure was solved by the direct method. Successive difference Fourier synthesis revealed all atoms. The structure was refined by the least-squares method on F^2. All atoms were refined anisotropically. For the anisotropic displacement parameters, the U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 1. Crystal Data for $[Cs][(SO_2)_2N_3^-$

chemical formula	Cs N3 O4 S2
fw	303.06
T, K	130(2)
space group	$P2_1/c$ (No. 14)
a, Å	8.945(2)
b, Å	10.454(2)
c, Å	8.152(2)
β, deg	109.166(3)
V, Å^3	720.0(2)
Z	4
ρ_{calcd}, g cm^{-3}	2.796
μ, mm^{-1}	5.685
R1,^{a} wR2^b [$I > 2\sigma(I)$]	0.0329, 0.0822
R1,^{a} wR2^b (all data)	0.0333, 0.0826

^{a} $R1 = (\sum(F_o - F_c)/F_o)$. ^{b} $wR2 = [\sum(w(F_o - F_c)^2)w/F_o{}^2)]^{1/2}$.

Results and Discussion

Preparation and Crystal Growth of $[Cs][(SO_2)_2N_3]$. Yellow 2:1 adducts of SO_2 and either CsN_3 or $[N(CH_3)_4][N_3]$ precipitate from their SO_2 solutions at low temperature.[12] While the $[N(CH_3)_4][(SO_2)_2N_3]$ salt is only marginally stable in a dynamic vacuum at −64 °C, that is, close to the freezing point of the SO_2 solvent, the corresponding Cs^+ salt is stable in a dynamic vacuum up to −30 °C.

Crystal Structure of $[Cs][(SO_2)_2N_3]$. Details of the crystal data for $[Cs][(SO_2)_2N_3]$ are provided in Table 1; the observed bond lengths, angles, and contacts are listed in Table 2, together with the geometric parameters previously calculated[12] for the $(SO_2)_2N_3^-$ anion. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table 3.

The $[Cs][(SO_2)_2N_3]$ salt crystallizes in the monoclinic space group $P2_1/c$ and contains the $(SO_2)_2N_3^-$ anion (Figure 1). The $(SO_2)_2N_3^-$ anions form double-layered sheets in the *bc*-plane, with half of the SO_2 groups in the center and the azide groups on the perimeters of the sheets (Figure 2). The Cs^+ cations are located within the sheets close to the perimeters and form contacts to the terminal azide nitrogen of the adjacent double-layers.

In the $(SO_2)_2N_3^-$ anion, the two SO_2 groups are bound to the same terminal nitrogen atom of N_3^-. The azide group is essentially linear with a significant difference in the N−N bond lengths (1.141(6) and 1.219(6) Å), which are very similar to those found in $[N(CH_3)_4][SO_2N_3]$ (1.144(2) and 1.214(2) Å).[11] In the $(SO_2)_2N_3^-$ anion, one S−N bond (2.201(5) Å) is significantly shorter than the second one (2.427(4) Å). However, both S−N bonds are longer than that found for the $SO_2N_3^-$ anion in $[N(CH_3)_4][SO_2N_3]$ (2.005(2) Å).[11] The marked difference between the S−N bond lengths

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Table 2. Experimental Bond Lengths [Å], Angles [deg], and Contacts [Å] for $[Cs][(SO_2)_2N_3]$ and Calculated[12] Bond Lengths and Angles for the $(SO_2)_2N_3^-$ Anion

	observed	calculated	
		B3LYP/6-31+G(d)	MP2/6-31+G(d)
N(2)−N(3)	1.141(6)	1.16	1.20
N(1)−N(2)	1.219(6)	1.21	1.23
S(1)−N(1)	2.201(5)	2.37	2.46
S(2)−N(1)	2.427(4)	2.40	2.48
S(1)−O(2)	1.449(4)	1.49	1.49
S(1)−O(1)	1.460(3)	1.48	1.49
S(2)−O(3)	1.433(4)	1.48	1.49
S(2)−O(4)	1.439(4)	1.48	1.49
N(1)−N(2)−N(3)	177.6(5)	178.9	177.5
S(1)−N(1)−S(2)	109.8(2)	117.5	100.7
N(2)−N(1)−S(1)	108.5(3)	108.7	102.3
N(2)−N(1)−S(2)	102.6(3)	112.9	99.3
O(2)−S(1)−O(1)	114.1(2)	115.2	116.3
O(3)−S(2)−O(4)	115.9(2)	115.5	116.3
O(2)−S(1)−N(1)	99.9(2)		
O(1)−S(1)−N(1)	97.1(2)		
O(3)−S(2)−N(1)	96.5(2)		
O(4)−S(2)−N(1)	96.3(2)		

Observed Contacts

N(3)···Cs(1A)	3.377(4)	N(3)···Cs(1B)	3.434(4)
N(3)···Cs(1C)	3.548(4)	N(1)···Cs(1F)	3.351(4)
O(1)···Cs(1)	3.807(4)	O(1)···Cs(1D)	3.114(3)
O(2)···Cs(1)	3.287(3)	O(2)···Cs(1B)	3.139(3)
O(3)···Cs(1C)	3.176(3)	O(3)···Cs(1E)	3.430(3)
O(4)···Cs(1F)	3.243(4)	O(4)···Cs(1G)	3.329(3)

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[Cs][(SO_2)_2N_3^-$

	x	*y*	*z*	*U*(eq)[a]
Cs(1)	2061(1)	768(1)	8967(1)	18(1)
S(1)	5507(1)	2332(1)	7631(2)	17(1)
S(2)	7207(1)	5091(1)	10692(2)	18(1)
O(3)	8352(4)	4630(3)	12259(4)	24(1)
O(4)	7694(5)	6163(3)	9883(5)	28(1)
O(1)	4375(4)	3355(3)	7554(5)	25(1)
O(2)	5671(4)	1419(3)	9016(5)	24(1)
N(3)	9574(5)	2165(4)	10774(6)	26(1)
N(2)	8664(5)	2788(3)	9789(5)	20(1)
N(1)	7672(5)	3467(4)	8786(6)	25(1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

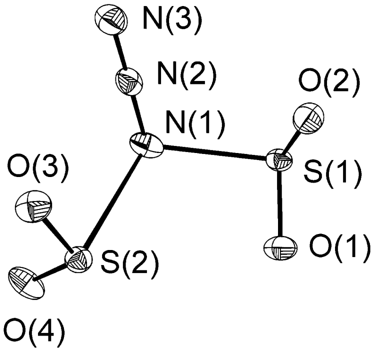

Figure 1. Structure of the $(SO_2)_2N_3^-$ ion in $[Cs][(SO_2)_2N_3]$. Thermal ellipsoids are shown at the 50% probability level.

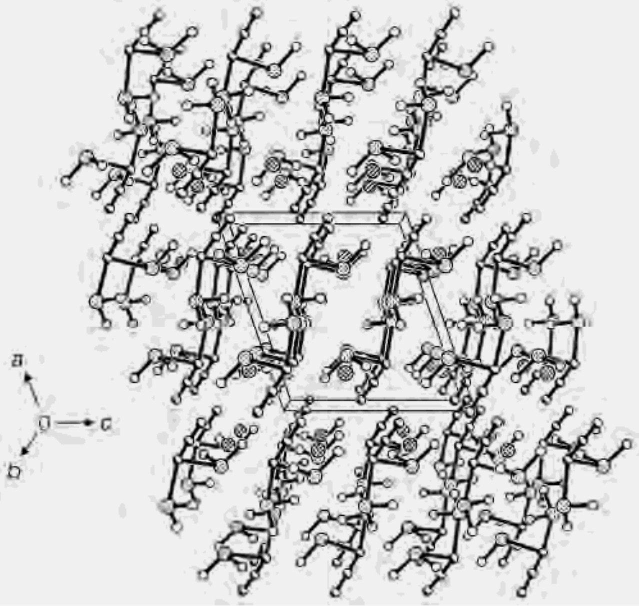

Figure 2. View of the packing of $[Cs][(SO_2)_2N_3]$ along the *b*-axis.

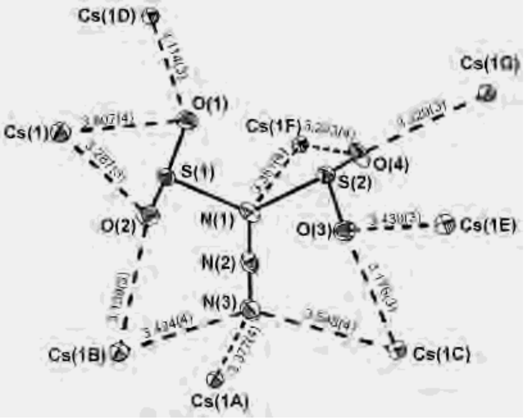

Figure 3. Closest interionic contacts (Å) in $[Cs][(SO_2)_2N_3]$. Thermal ellipsoids are shown at the 50% probability level.

observed for the two SO_2 ligands in $(SO_2)_2N_3^-$ is in contrast to the calculated structure of the free gaseous anion, in which both SO_2 ligands exhibit similar S−N distances. The differences between the observed solid state and the calculated gas-phase structures are likely due to packing effects and anion−cation interactions in the solid state. The Cs^+ cation forms strong interionic contacts to N(1), N(3), and the oxygen atoms of the anion which are as short as 3.114(3) Å (Figure 3). Because of the weakness of the N−S bonds, the orientation of the SO_2 groups in the $(SO_2)_2N_3^-$ anion is largely governed by the contacts to the Cs^+ cations. The agreement between the calculated and observed structures of the $(SO_2)_2N_3^-$ anion is quite good considering the weak S−N bonds and the strong anion−cation interactions.

The observed structure of the 1,1-$(SO_2)_2N_3^-$ anion is in agreement with the previous predictions[12] which were based on the experimental vibrational spectra of the Cs^+ and $N(CH_3)_4^+$ salts. The 1,1-isomer has been calculated to be more stable than the 1,3-$(SO_2)_2N_3^-$ anion by 3.5 (0.4) kcal/mol at the B3LYP (MP2) level of theory.[12] Preferential 1,1-coordination has also been observed for the $H_2N_3^+$ cation[20] and dinuclear metal azide complexes.[21]

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Conclusions. At low temperature, yellow $[Cs][(SO_2)_2N_3]$ crystallizes from a solution of CsN_3 in liquid SO_2. The crystal structure of $[Cs][(SO_2)_2N_3]$ contains the $(SO_2)_2N_3^-$ anion in which both SO_2 ligands are coordinated to the same terminal nitrogen. This study provides the first crystal structure of a halide or pseudohalide anion bound to more than one SO_2 ligand.

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Supporting Information Available: Additional tables in PDF format. Tables of structure determination summary, atomic coordinates, bond lengths and angles and anisotropic displacement parameters of $[Cs][(SO_2)_2N_3]$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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