REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
	Technical Paper	

4. TITLE AND SUBTITLE

5a. CONTRACT NUMBER
F0461-99-C-0025

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

ERC

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

20020830 102

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Leilani Richardson
Unclassified	Unclassified	Unclassified	A		19b. TELEPHONE NUMBER *(include area code)* (661) 275-5015

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

2 items enclosed

FILE

MEMORANDUM FOR PRS (In-House/Contractor Publication)

FROM: PROI (STINFO) 05 August 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2002-197**
Karl Christe (ERC) et al., "The $(SO_2)_2N_3^-$ Anion"

55194

Inorganic Chemistry **(Statement A)**
(Deadline: N/A)

submitter =

The $(SO_2)_2N_3^-$ Anion

Karl O. Christe,*[†,‡] Michael Gerken,[†,¶] Ralf Haiges,[†] Stefan Schneider,[†] Thorsten Schroer,[†] Irena Tsyba,[†] Robert Bau[†]

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089, and Propulsion Sciences and Advanced Concepts Division, Air Force Research Laboratory, Edwards AFB, California 93524

Abstract: 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, $\hat{a}$ = 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 non-aqueous inorganic solvent.[1-3] 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 found to form adducts with SO_2 in a 1:1 ratio. These adducts can be viewed as halosulfites and pseudohalosufites. The strength of the bond between the anions and SO_2 was found to decrease with increasing anion size.[6,11,13] In the SO_2F^- anion, the S-F bonds is basically a single bond, while the S-anion bonds in SO_2I^- and SO_2SCN^- are best described as contacts or secondary bonds. In a recent paper in this journal, we reported the

synthesis of $[M][SO_2N_3]$ and $[M][(SO_2)_2N_3]$, M = $N(CH_3)_4$ and Cs and their characterization by NMR and vibrational spectroscopy.[12] The $[M][(SO_2)_2N_3]$ salts represent the first spectroscopically characterized adduct of SO_2 with an anion in a 2:1 ratio in the solid state.[12] Vibrational spectroscopy of N_3^- in SO_2 solution indicates the presence of the $(SO_2)_2N_3^-$ anion.[12] 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 counter-cation. However, no structural information was obtained.[14] A UV and infrared spectroscopic study of halides and halosulfites in SO_2 solution provided evidence for the presence of 2:1 adducts. The structure proposed for the $(SO_2)_2X^-$ anion involved an O_2S-SO_2 moiety, coordinated to the halide 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.

Experimental Section

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

Materials and Apparatus. Reactions were carried out in Teflon-FEP ampoules 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 glove box. 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 dry box, approximately 0.02g 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" 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 ampoule 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 MoK_α radiation (λ = 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 ten-second 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.

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, *i. e.*, 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 (Fig. 1). The $(SO_2)_2N_3^-$ anions form in 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

(Fig. 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 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 (Fig. 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]

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.

Acknowledgements

The authors thank the National Science Foundation, the Defense Advanced Projects Agency, and the Air Force Office of Scientific Research for financial support. M. G. thanks the Natural Sciences and Engineering Research Council of Canada for a postdoctoral fellowship, and R. H. , the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship.

Supporting Information Available

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.

References

* To whom correspondence should be sent. E-mail: karl.christe@edwards.af.mil.

† University of Southern California

‡ Air Force Research Laboratory

¶ Present address: Department of Chemistry and Biochemistry, The University of Lethbridge, Alberta, T1K 3M4, Canada

(1) Waddington, T. C. In *Nonaqueous Solvent Systems*; Waddington, T. C., Ed.; Academic Press: London, 1965; p. 253.

(2) Karcher, W.; Hechts, H. In *Chemistry in Nonaqueous Ionizing Solvent*, Vol. 3; Jander, G.; Spandou, J., Addison, C. C., Eds.; Pergamon: Oxford, 1967; p. 79.

(3) Burow, D. F. In *Nonaqueous Solvents*; Lagowski, J. J., Ed.; Academic Press: New York, 1970; p. 138.

(4) Mews, R.; Lork, E.; Watson, P. G. Görtler, B. *Coord. Chem. Rev.* **2000**, *197*, 277.

(5) (a) Kornath, A.; Neumann, F.; Ludwig, R. *Inorg. Chem.* **1997**, *36*, 5570; (b) Lork, E.; Mews, R.; Viets, D.; Watson, P. G.; Borrmann, T.; Vij, A.; Boatz, J.; Christe, K. O. *Inorg. Chem.* **2001**, *40*, 1303; (c) Kessler, U.; van Wüllen, L.; Jansen, M. *Inorg. Chem.* **2001**, *40*, 7040.

(6) Burow, D. F. *Inorg. Chem.* **1972**, *11*, 573.

(7) Kuhn, N.; Bohnen, H.; Bläser, D.; Boese, R., Maulitz, A. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2283.

(8) (a) Snow, M. R.; Ibers, J. A. *Inorg. Chem.* **1973**, *12*, 224; (b) Ellers, P. G.; Kubas, G. J. *Inorg. Chem.* **1978**, *17*, 894.

(9) Kornath, A.; Blecher, O.; Ludwig, R. *J. Am. Chem. Soc.* **1999**, *121*, 4019.

(10) Kornath, A.; Blecher, O.; Ludwig, R. *Z. Anorg. Allg. Chem.* **2000**, *626*, 731.

(11) Kornath, A.; Blecher, O.; Ludwig, R. *Z. Anorg. Allg. Chem.* **2002**, *628*, 183.

(12) Christe, K. O.; Boatz, J. A.; Gerken, M.; Haiges, R; Schneider, S.; Schroer, S.; Tham, F. S.; Vij, A.; Vij, A.; Wagner, R. I.; Wilson W. W. *Inorg. Chem.* **2002** In press.

(13) Maulitz, A. H.; Boese, R.; Kuhn, N. *J. Mol. Struct.* **1995**, *333*, 227.

(14) Jander, G.; Mesech, H. *Z. Phys. Chem., Abt. A*, **1938**, *183*, 121.

(15) Gerken, M.; Schneider, S.; Schroer, T.; Haiges, R.; Christe, K. O. *Z. Anorg. Allg. Chem.* **2002**, *628*, 909.

(16) SMART V 5.625, Software for the CCD Detector System, Bruker AXS, Madison, WI, 2001.

(17) SAINT V 6.22, Software for the CCD Detector System, Bruker AXS, Madison, WI, 2001.

(18) SADABS, Program for absorption correction for area detectors, Version 2.03, Bruker AXS, Madison, WI (2001).

(19) SHELXTL 6.10 for Windows NT, Program library for Structure Solution and Molecular Graphics, Bruker AXS, Madison, WI (2000).

(20) Christe, K. O.; Wilson, W. W.; Dixon, D. A.; Khan, S. I.; Bau, R.; Metzenthin, T.; Lu, R. *J. Am. Chem. Soc.* **1993**, *115*, 1836.

(21) Kornath, A. *Angew. Chem.* **2001**, *113*, 3231; *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 3135.

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_{calc}, g cm^{-3}	2.796
μ, mm^{-1}	5.685
R1,[a] *wR2*[b] [I > 2ó(I)]	0.0329, 0.0822
R1,[a] *wR2*[b] (all data)	0.0333, 0.0826

---

[a] $R1 = (\Sigma(F_0-F_c)/F_0)$. [b] $wR2 = [\Sigma(w(F_0-F_c)^2)w/F_0^2)]^{1/2}$.

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

		calcd.	
	obsd.	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)		
obsd. 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 (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 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)

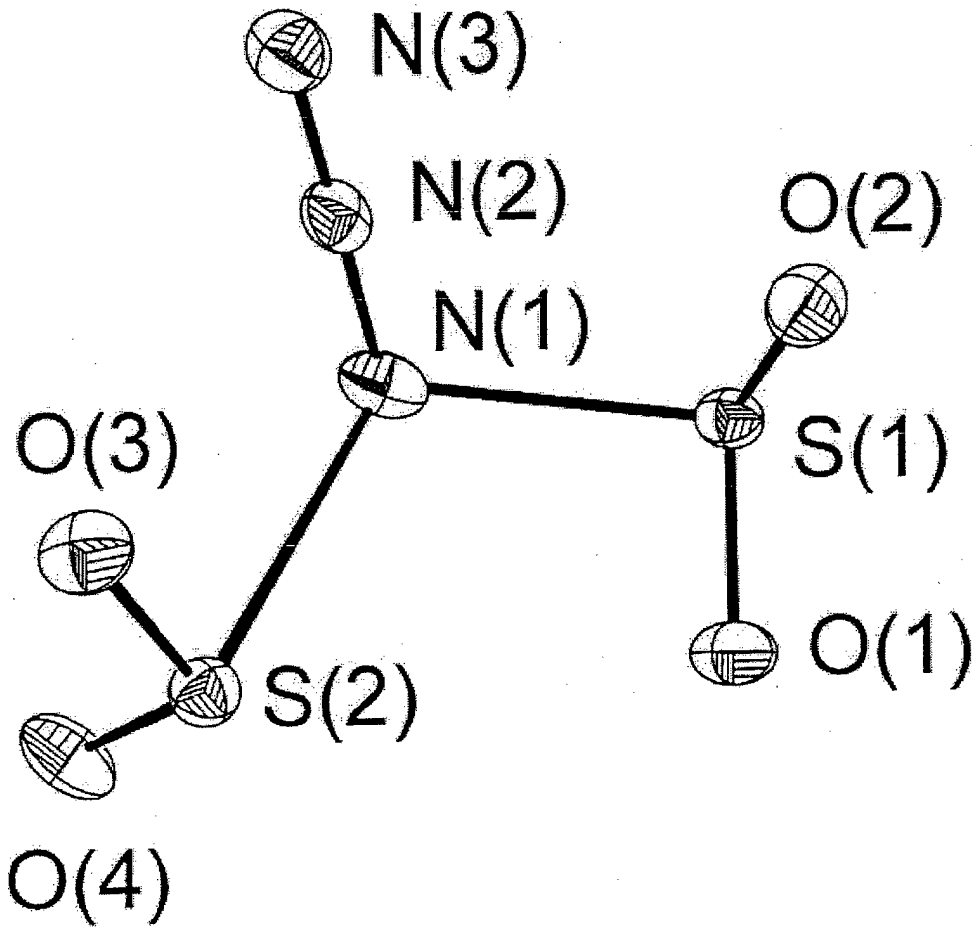
[a] U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

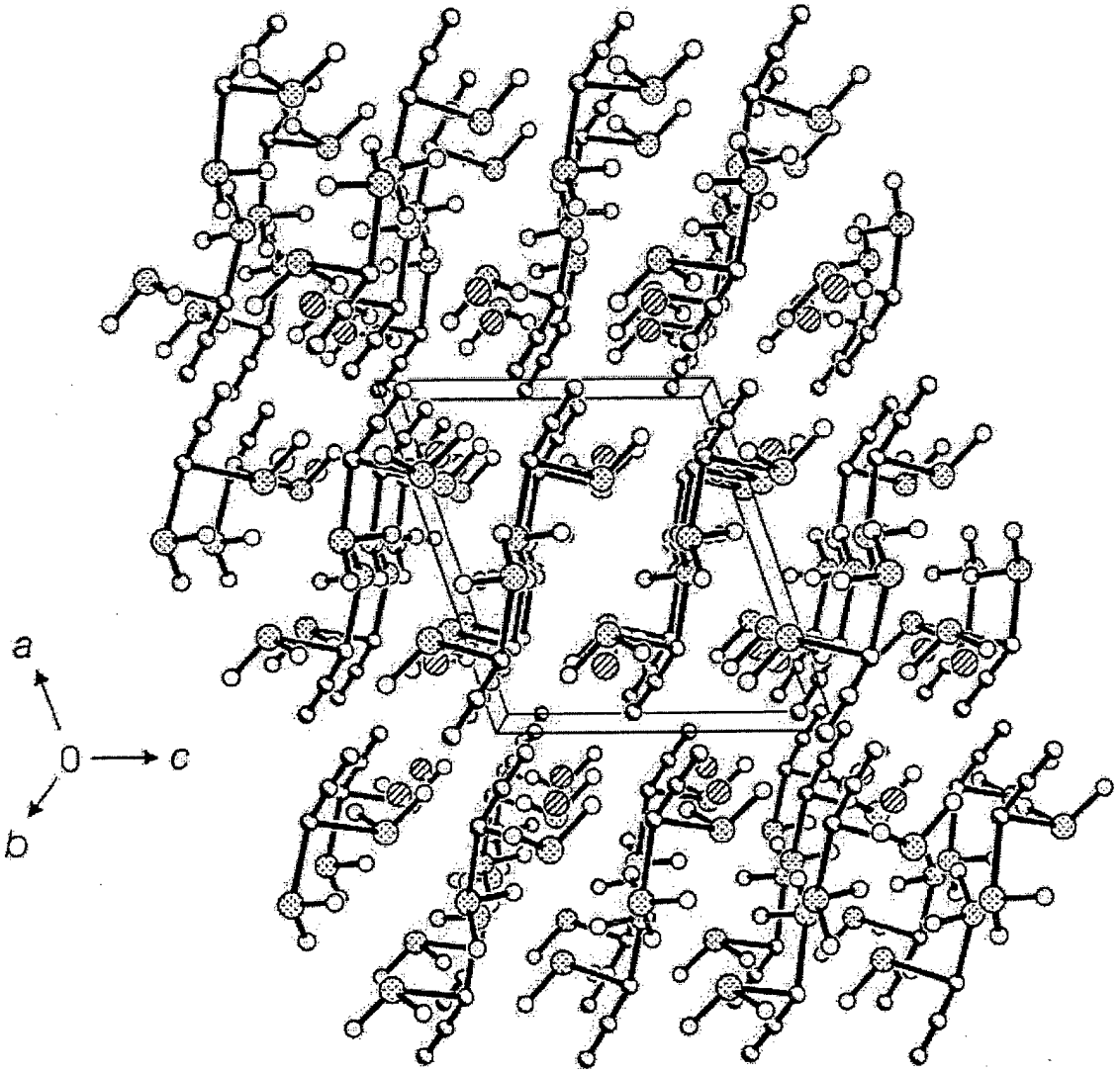
Figure Captions

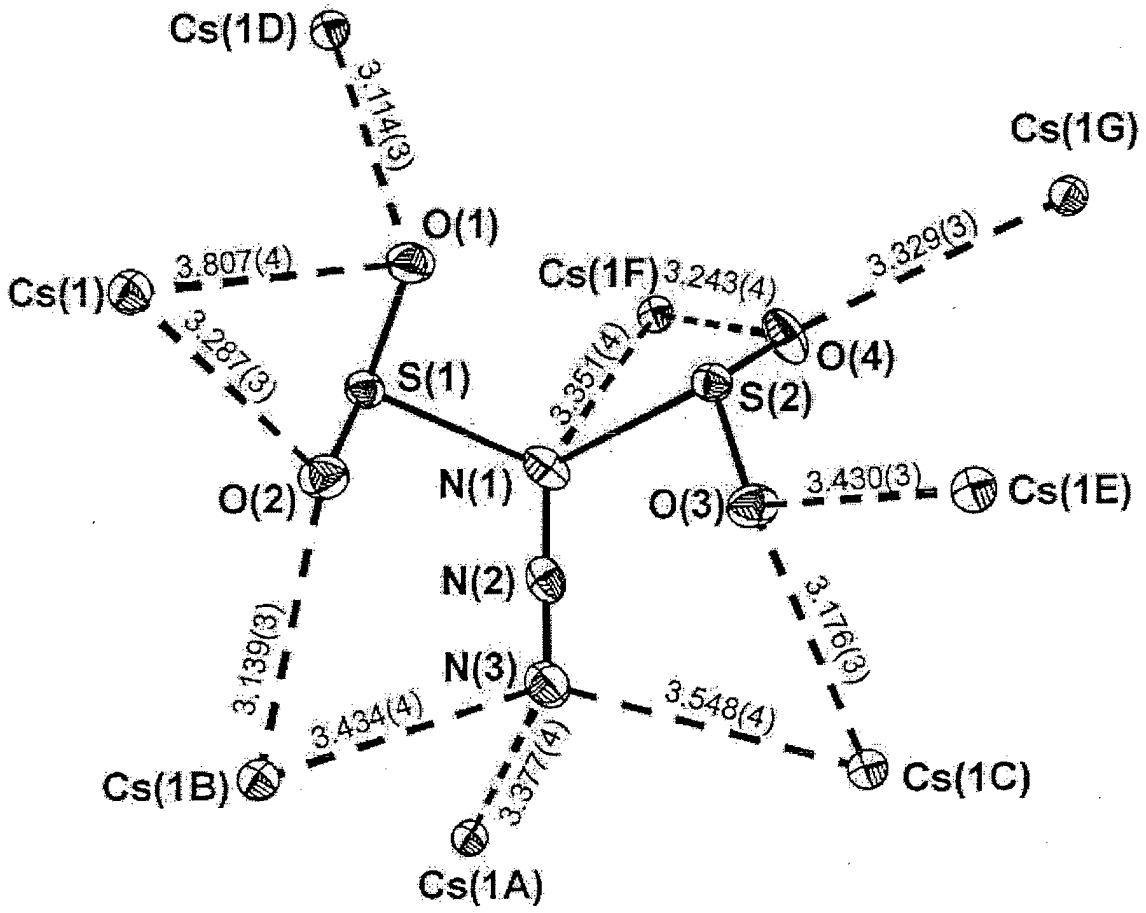
Figure 1. Structure of the $(SO_2)_2N_3^-$ ion in $[Cs][(SO_2)_2N_3]$. Thermal ellipsoids are shown at the 50% probability level.

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.


N(3)
N(2)
O(2)
N(1)
O(3)
S(1)
O(1)
S(2)
O(4)


a
0
c
b


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

The $(SO_2)_2N_3^-$ Anion

Karl O. Christe,* Michael Gerken, Ralf Haiges, Stefan Schneider, Thorsten Schroer, Irena Tsyba, and Robert Bau

The recently reported 2:1 adduct between SO_2 and the N_3^- anion, $(SO_2)_2N_3^-$, is structurally characterized by single crystal X-ray diffraction of the $[Cs][(SO_2)_2N_3]$ salt. The crystal structure establishes the 1,1-coordination of two SO_2 ligands to the N_3^- anion.