The oxygen atoms are the acceptors in H bonds formed by the amine groups of urea molecules belonging to the neighboring dimers (Table III). Distances between the N and Cl atoms suggest H bonds within the dimers and between them. However, the calculated positions of H atoms indicate that there are only the intracomplex N–H···Cl bonds.

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Registry No. UMC, 86064-71-3; urea, 57-13-6.

Supplementary Material Available: Tables of anisotropic atomic thermal motion parameters, calculated atomic positional coordinates for hydrogen atoms, nonessential angles, equations of planes, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Preparation and Crystal Structure of $\{Zn[S(NSO)_2]_2\}(AsF_6)_2 \cdot 2SO_2$: A Compound with a Two-Dimensional Network through Oxygen Atoms

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Bis(sulfinylamino) sulfide, $S(NSO)_2$, was first prepared by Goehring and Heinke.[1] X-ray analysis showed a noncyclic arrangement of the atoms.[2] Reactions of $S(NSO)_2$ are only known with nonmetallic elements or compounds. It was shown that $S(NSO)_2$ reacts with silicon–nitrogen compounds with cleavage of the Si–N bond and formation of compounds containing the sulfoximide group.[3] Herein we report the first example where $S(NSO)_2$ functions as a ligand in metal complexes.

Experimental Section

The compound $S(NSO)_2$ may be prepared from ammonia and thionyl chloride[1] or by the reaction of $(CH_3)_3SiNSO$ and sulfur dichloride.[4]

Preparation of Bis[bis(sulfinylamino)sulfido]zinc(II) Bis[hexafluoroarsenate(V)]–Bis(sulfur dioxide). A 3.2-g amount (5 mmol) of $[Zn(SO_2)_2](AsF_6)_2$[7] and 1.74 g (11 mmol) of $S(NSO)_2$[4] were placed in a pressure flask and cooled to −78 °C. Twenty milliliters of SO_2 was added. The solution was allowed to warm to room temperature and was stirred for 12 h. After removal of SO_2, the bright yellow residue was washed with dry methylene chloride several times and recrystallized from liquid SO_2: dec pt 170–185 °C; yield 4.19 g (95%). Anal. Calcd for $\{Zn[S(NSO)_2]_2\}(AsF_6)_2 \cdot 2SO_2$: F, 25.8; S, 28.9; N, 6.3. Found: F, 27.1; S, 27.9; N, 6.7.

Table I. Crystal Data and Structure Analysis

space group	$P2_1/n$
a, Å	8.442 (1)
b, Å	13.106 (2)
c, Å	10.997 (1)
β, deg	101.47 (1)
V, Å^3	1192.3 (5)
cryst dimens, mm	0.30 × 0.35 × 0.55
D_{calcd}, g cm^{-3}	2.461
total no. of reflctns	5665
no. of indep reflctns	2731
$I > 0.3\sigma(I)$	2600
$[(\sin\theta)/\lambda]_{max}$	0.65
$R(F)$	0.051
$R_w(F)$	0.059

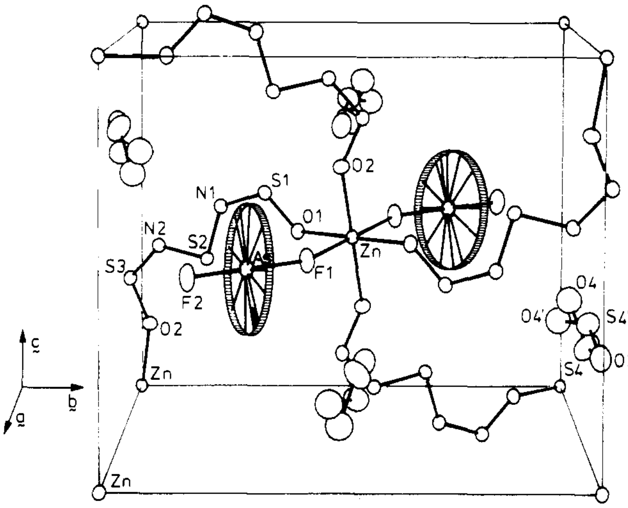

Figure 1. View of the crystal structure of the title compound. The positions of the 14 fragments of the four fluorine atoms are represented by a wheel. The two positions of the split atoms of the SO_2 group are included.

Crystal Structure Determination. A yellow crystal was sealed in a glass capillary to prevent it from decomposing in the air. The cell constants were determined on an Enraf-Nonius CAD4 diffractometer from 25 well-centered reflections. The systematic extinctions correspond to space group $P2_1/n$; the cell volume corresponds to two formula units. Reflections were collected with an ω-scan and Mo $K\alpha$ radiation (graphite monochromator) at 298 K in two quadrants of reciprocal space up to 2θ = 50 and 55°, respectively. Data were rescaled with respect to an intensity decrease of about 4% of the standard reflections. An empirical absorption correction based on ψ-scans of four reflections gave maximum differences in transmission of 18%.[5] Equivalent reflections were averaged ($R(I)_{internal}$ = 0.018), and all observations with $I > 0.3\sigma(I)$ were used in the analysis. For further details see Table I.

The structure was determined by Patterson and Fourier techniques. In the course of the structure determination it was found that the $[AsF_6]^-$ and SO_2 groups were disordered. For the $[AsF_6]^-$ group only two fluorine atoms are well localized (the axial atoms F(1) and F(2)), while a smeared ring of electron density ranging between 2.5 and 4.5 e/Å^3 was observed about the F(1)–As–F(2) axis. Consequently the group was supposed to be considerably disordered or to rotate about this axis. The problem was overcome by describing the ring of F atoms by a large number of partly occupied atoms (14 fragments). The positions of these fragments are represented in Figure 1 in the form of a wheel. Their positional parameters, occupation numbers, and isotropic temperature factors are included in the supplementary material. The structure analysis does not allow us to distinguish between rotational or static disorder of this group. For the SO_2 group only the O(3) atom was well localized, while two positions were found for both S(4) and O(4). These atoms were described with a split-atom model. Both positions for the disordered atoms are included in Figure 1; they are labeled S(4), S(4′), O(4), and O(4′). Atomic scattering factors and anomalous dispersion factors were taken from ref 6. The

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Table II. Positional Parameters

atom	*x*	*y*	*z*
As	0.27017 (6)	0.21813 (4)	−0.02812 (5)
Zn	0.0	0.0	0.0
S(1)	0.3214 (2)	0.30332 (9)	0.5834 (1)
S(2)	0.2933 (1)	0.66605 (9)	0.1104 (1)
S(3)	0.0693 (2)	0.97872 (9)	0.3093 (1)
S(4)[a]	0.4679 (5)	0.9892 (4)	0.7677 (4)
S(4′)[a]	0.4278 (6)	0.9901 (4)	0.7004 (5)
F(1)	0.3102 (4)	0.5950 (2)	0.5221 (3)
F(2)	0.1500 (5)	0.8356 (3)	0.5335 (4)
O(1)	0.1576 (4)	0.8777 (2)	0.0127 (3)
O(2)	0.0626 (5)	0.0234 (3)	0.1859 (3)
O(3)	0.3086 (7)	0.9748 (4)	0.7585 (5)
N(1)	0.2462 (5)	0.7006 (3)	0.9642 (3)
N(2)	0.3584 (5)	0.5506 (3)	0.0868 (3)
O(4)[a]	0.515 (2)	1.024 (1)	0.660 (1)
O(4′)[a]	0.563 (2)	1.044 (1)	0.723 (1)

[a] Population 0.5.

Table III. Bond Distances (Å) and Angles (deg)

Zn–O(1) (2×)	2.070 (2)	S(3)–O(2)	1.468 (2)
Zn–O(2) (2×)	2.030 (2)	As–F(1)	1.756 (2)
Zn–F(1) (2×)	2.082 (2)	As–F(2)	1.687 (2)
S(1)–O(1)	1.475 (2)	S(4)–O(3)	1.341 (6)
S(1)–N(1)	1.514 (3)	S(4)–O(4)	1.39 (1)
S(2)–N(1)	1.641 (3)	S(4′)–O(3)	1.310 (7)
S(2)–N(2)	1.647 (3)	S(4′)–O(4′)	1.32 (1)
S(3)–N(2)	1.513 (3)		

O(1)–Zn–O(1)	180.0	Zn–O(1)–S(1)	129.1 (1)
O(1)–Zn–O(2) (2×)	90.8 (1)	Zn–O(2)–S(3)	145.6 (2)
O(1)–Zn–O(2) (2×)	89.2 (1)	O(1)–S(1)–N(1)	115.5 (1)
O(1)–Zn–F(1) (2×)	91.6 (1)	N(1)–S(2)–N(2)	97.0 (1)
O(1)–Zn–F(1) (2×)	88.4 (1)	N(2)–S(3)–O(2)	112.7 (2)
O(2)–Zn–O(2)	180.0	S(1)–N(1)–S(2)	125.9 (2)
O(2)–Zn–F(1) (2×)	91.4 (1)	S(2)–N(2)–S(3)	123.3 (2)
O(2)–Zn–F(1) (2×)	88.6 (1)	Zn–F(1)–As	150.0 (2)
F(1)–Zn–F(1)	180.0	F(1)–As–F(2)	179.2 (1)
O(3)–S(4)–O(4)	116 (1)	O(3)–S(4′)–O(4′)	135 (1)

Table IV. Shortest Contact Distances (Å)

	Intermolecular		
S(1)···O(2)	3.109 (2)	S(3)···O(3)	3.188 (3)
S(1)···O(3)	3.167 (3)	S(3)···O(4′)	3.21 (1)
S(3)···F(2)	3.065 (2)		
	Intramolecular		
S(2)···O(2)	2.985 (2)	S(2)···O(1)	3.110 (2)

final refinement, including isotropic extinction, resulted in $R(F) = 0.051$ and $R_w(F) = 0.059$. These values are larger than expected from the quality of the data, due to the difficulty in describing the disordered atoms. The final difference synthesis did not show peaks exceeding 0.7 e/Å^3. The atomic parameters are given in Table II.

Results and Discussion

The reaction of $[Zn(SO_2)_2](AsF_6)_2$ and $S(NSO)_2$ in a molar ratio of 1:2 in liquid SO_2 results in the formation of a complex with the composition $\{Zn[S(NSO)_2]_2\}(AsF_6)_2 \cdot 2SO_2$ (**1**). $S(NSO)_2$ was prepared from $(CH_3)_3SiNSO$ and sulfur dichloride.[4] **1** forms bright yellow crystals, which are stable under an SO_2 atmosphere but decompose in moist air. **1** starts to lose SO_2 at room temperature, which results in the decomposition of the surface and formation of $\{Zn[S(NSO)_2]_2\}(AsF_6)_2$. The crystal itself starts to decompose at 170 °C. **1** was characterized by an X-ray single-crystal structure investigation.

From previous structural investigations it was shown that $S(NSO)_2$ has an open-chain structure. The Zn^{2+} ion may be bonded by the sulfur, nitrogen, or oxygen atoms. Furthermore, $S(NSO)_2$ may function as a bidentate chelating or bidentate bridging group. On the basis of vibrational spectroscopy an unambiguous structural assignment could not be made. The S=O and S=N stretching frequencies fall into the same region.

Bond distances and angles are reported in Table III; a view of the structure is shown in Figure 1. The Zn atom, which is located at the inversion center, has an octahedral coordination. It is coordinated by four O atoms from different, but crystallographically related, $S(NSO)_2$ groups and by two F atoms from $(AsF_6)^-$ groups. The Zn–O distances of 2.030 (2) and 2.070 (2) Å are in good agreement with similar values in $[Zn(S_3N_2O)_6]^{2+}$.[7]

The Zn–F distance is 2.082 (2) Å. It can be compared with values of 1.97 Å in $ZnPtF_6$,[8] 2.10 Å in $ZnSnF_6$,[9] 2.07 Å in $ZnPdF_6$,[10] and 2.03 Å in $ZnF_2 \cdot 4H_2O$.[11]

The $S(NSO)_2$ groups form chains between the Zn atoms, leading to a two-dimensional network in the $\bar{1}01$ plane.

The S(1)–N(1) and S(3)–N(2) bonds of 1.514 (3) and 1.513 (3) Å correspond to double bonds. The two S–N bonds involving S(2) are slightly shorter than single bonds.

The S–O bonds of 1.468 (2) and 1.475 (2) Å are comparable with the double-bond length in sulfates. The O=S=N—S groups have the cis configuration and do not deviate significantly from planarity.

The entire $S(NSO)_2$ group is rather planar. The largest deviation from planarity is given by S(2) and is 0.067 (1) Å. In the comparison of these values with the structural data of the free ligand[2] it is interesting to note that in **1** all bond distances are longer except the two S–N bonds involving S(2). The O(1)–S(1)–N(1) angle is similar as in the free ligand while the S(1)–N(1)–S(2) and N(1)–S(2)–N(2) angles are slightly enlarged. The crystal packing shows a number of intermolecular interactions that are slightly shorter (up to 0.15 Å) than the sum of the van der Waals radii of the atoms. They are reported in Table IV and are of the type S···O and S···F. In addition the diffuse ring of fluorine atoms approaches the S(1) and S(4) atoms up to 2.9 Å and thus may contribute to the crystal packing in the form of van der Waals contacts.

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Registry No. **1**, 85940-01-8; $[Zn(SO_2)_2](AsF_6)_2$, 83778-97-6; $S(NSO)_2$, 77133-46-1.

Supplementary Material Available: Listings of anisotropic temperature factors, observed and calculated structure factor amplitudes, deviations from least-squares planes, and parameters of the fluorine fragments (15 pages). Ordering information is given on any masthead page.

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Biological Analogues. Synthesis of Vicinal Trimercapto Ligands

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The current interest in the synthesis of low molecular weight structural analogues of the protein metal binding sites of, among others, the nitrogenases,[1,2] ferredoxins,[3] metallo-