

Dithiocarbimates from Sulfonamides, Part 1: Preparation and X-Ray Crystal Structures of $K_2[S_2C=N-SO_2-C_6H_5] \cdot 2 H_2O$ and $K_2[S_2C=N-SO_2-C_6H_4-Cl] \cdot 2 H_2O$

Hans-Ulrich Hummel* and Uwe Korn

Institut für Anorganische Chemie der Universität, Egerlandstraße 1, D-8520 Erlangen

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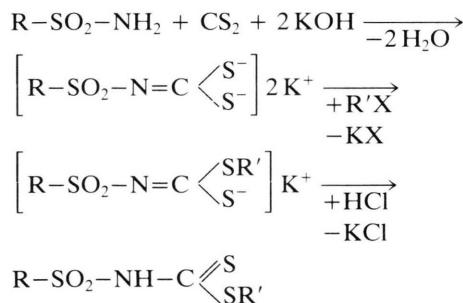
Dithiocarbimates, Sulfonamides, X-Ray, Sulfones

By reaction of the sulfonamides $C_6H_5-SO_2-NH_2$ and $p-Cl-C_6H_4-SO_2-NH_2$ with CS_2 in the presence of bases the corresponding dithiocarbimates have been obtained in form of their potassium salts and characterized by means of X-ray structural analysis. Both compounds crystallize in the space group $P2_1/a$ with $a = 29.778(3)$, $b = 6.202(1)$, $c = 7.169(1)$ Å and $\beta = 90.33(2)^\circ$ for $K_2[S_2C=N-SO_2-C_6H_5] \cdot 2 H_2O$ and $a = 31.517(3)$, $b = 7.189(1)$, $c = 6.196(1)$ Å and $\beta = 90.10(1)^\circ$ for the Cl-substituted species, respectively. A relation between both crystal structures becomes obvious when for $K_2[S_2C=N-SO_2-C_6H_4-Cl] \cdot 2 H_2O$ the first space group setting is chosen; *i.e.* $P112_1/a$. The dithiocarbimates are built up of two planar moieties. One plane contains the $S_2C=N-SO$ framework of each anion while a second plane consists of the $S-C_6H_5$ group and the $S-C_6H_4-Cl$ group, respectively. The two planes are oriented nearly perpendicular to each other and give rise to conjugation involving the SO_2 groups in the different systems.

Introduction

Dithiocarbamates $(R_2NCS_2)^-$ are well characterized compounds due to their use in industrial processes and their biological activities [1]. The electrochemistry of dithiocarbamate complexes with transition metals has been investigated in some detail with respect to unusual oxidation states of the involved metals [2]. Nevertheless the chemistry of the related dinegative dithiocarbimates $(RNCS_2)^{2-}$ has not been studied to a great extent, and only complexes of the ligand $[(NC)NCS_2]^{2-}$ and the bis-nickel complex of $(PhNCS_2)^{2-}$ have been reported [1, 3]. Although dithiocarbimates are frequently used in organic synthesis as intermediates, there is a considerable lack of information on molecular structures, complex chemistry and redox behaviour of those systems [1, 3, 4].

The reaction of sulfonamides with CS_2 in the presence of bases give N-sulfonyl-dithiocarbimates which easily can be converted into N-sulfonyl-dithiourethanes:



Our general interest in the chemistry of 1,1-dithiolates led us to carry out detailed investigations on substituted aryl-N-sulfonyl-dithiocarbimates $(p-R-C_6H_4-SO_2-N=CS_2)^{2-}$ ($R = H$: **1**, $R = Cl$: **2**, $R = CH_3$: **3**) [5–7].

In the present paper we report on the crystal structures of $K_2[S_2C=N-SO_2-C_6H_5] \cdot 2 H_2O$ and $K_2[S_2C=N-SO_2-C_6H_4-Cl] \cdot 2 H_2O$ in order to demonstrate the geometry of “uncomplexed” ligands, while in a subsequent paper ternary nickel-compounds with **1** and **2** are described.

Experimental

Preparation of $K_2 \mathbf{1} \cdot 2 H_2O$ and $K_2 \mathbf{2} \cdot 2 H_2O$

The starting materials were prepared according to procedures given in the literature [4]. Recrystallization from a water-aceton-methanol mixture (1:20:2) gave pale yellow plates in 75–80% yield.

* Reprint requests to Dr. Hans-Ulrich Hummel.

X-ray structure analysis

Space groups of both compounds have been obtained using film techniques (Weissenberg and precession methods, $\text{CuK}\alpha$ and $\text{MoK}\alpha$ radiation; systematic absences: $h0l$, $h = 2n+1$; $0k0$, $k = 2n+1$). Data collections were carried out at room temperature using graphite-monochromated four-circle diffractometers (HUBER, $\text{MoK}\alpha$: $\text{K}_2\mathbf{1} \cdot 2\text{H}_2\text{O}$; PHILIPS PW 1100, $\text{AgK}\alpha$: $\text{K}_2\mathbf{2} \cdot 2\text{H}_2\text{O}$). 25 reflections were used to determine the final lattice parameters. The data were corrected for decay (<0.1) by scaling on three standards and for Lorentz and polarization effects. Crystal structures were solved by using direct methods of the SHELXS-86 software system on a DEC Micro Vax II [8]. The full models of the structures were obtained by subsequent Fourier synthesis and least squares refinement using the SHELX-76 system [9]. All phenyl rings were refined as rigid bodies with fixed C—C distances of 1.39 Å and C—C—C angles of 120° . The positions of H atoms on the phenyl rings were calculated by using a fixed C—H distance of 0.96 Å.

Details concerning the crystal structure analysis have been collected in Table I, while Tables II and III contain atomic coordinates and temperature factors.

Table II. Atomic coordinates and equivalent temperature-factors for the nonhydrogen-atoms of

 $\text{K}_2[\text{S}_2\text{C}=\text{N}-\text{SO}_2-\text{C}_6\text{H}_5] \cdot 2\text{H}_2\text{O}$.

$$U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j \text{ (Å}^2\text{)}.$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
K1	0.3877(1)	0.8363(3)	0.2675(2)	0.0410(25)
K2	0.4700(1)	0.7698(3)	0.8510(3)	0.0420(25)
S1	0.3699(1)	0.3338(3)	0.3539(3)	0.0230(28)
S2	0.4558(1)	0.1611(4)	0.5062(3)	0.0348(28)
S3	0.3649(1)	0.5871(3)	0.7453(3)	0.0349(25)
C1	0.4079(2)	0.3202(11)	0.5315(9)	0.0284(59)
N	0.4058(2)	0.4244(10)	0.6953(8)	0.0303(56)
O1	0.3589(2)	0.7584(8)	0.6122(7)	0.0481(54)
O2	0.3753(2)	0.6583(9)	0.9324(7)	0.0510(56)
C21	0.3152(1)	0.4392(7)	0.7565(5)	0.0304(59)
C22	0.2756(1)	0.5279(7)	0.6854(5)	0.0346(61)
C23	0.2356(1)	0.4105(7)	0.6922(5)	0.0654(65)
C24	0.2353(1)	0.2044(7)	0.7701(5)	0.0873(64)
C25	0.2749(1)	0.1157(7)	0.8411(5)	0.0719(64)
C26	0.3148(1)	0.2331(7)	0.8343(5)	0.0445(62)
OW1	0.0602(2)	0.6602(9)	0.9908(7)	0.0358(55)
OW2	0.4725(2)	0.6174(8)	0.2216(7)	0.0497(55)

Table I. Crystallographic details for the structure determinations of $\text{K}_2\mathbf{1} \cdot 2\text{H}_2\text{O}$ and $\text{K}_2\mathbf{2} \cdot 2\text{H}_2\text{O}^*$.

Formula	$\text{K}_2[\text{S}_2\text{C}=\text{N}-\text{SO}_2-\text{C}_6\text{H}_5] \cdot 2\text{H}_2\text{O}$	$\text{K}_2[\text{S}_2\text{C}=\text{N}-\text{SO}_2-\text{C}_6\text{H}_4-\text{Cl}] \cdot 2\text{H}_2\text{O}$
M_r	345.54	378.99
<i>a</i> [Å]	29.778(3)	31.517(3)
<i>b</i> [Å]	6.202(1)	7.189(1)
<i>c</i> [Å]	7.169(1)	6.196(1)
β [°]	90.33(2)	90.10(1)
<i>V</i> [Å ³]	1323.97	1403.86
<i>Z</i>	4	4
d_x [g cm ⁻³]	1.73	1.79
Space group	$P2_1/a$ No. 14	$P2_1/a$ No. 14 [10]
Diffractometer	HUBER	PHILIPS
λ [Å]	$\text{MoK}\alpha$ -0.70926	$\text{AgK}\alpha$ -0.55970
Temperature [K]	293 ± 2	293 ± 2
θ -Range [°]	$2 \leq \theta \leq 25$	$2 \leq \theta \leq 18$
Total reflections	5566	5475
Symmetry-independent reflections	1758	2174
Observed reflections	1198 $F_o \geq 9\sigma(F)$	1584 $F_o \geq 6\sigma(F)$
Refinement	K1, K2, OW1, OW2, 1 , 2 : anisotropically. Phenylprotons: geometrically with common isotropic temperature-factor. Waterprotons from difference-fourier, unit-weights	
Number of parameters	159	165
$R = \sum F_o - F_c / \sum F_o $	0.045	0.032

* Additional crystal structure data have been deposited at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG. Inquiries should be accompanied by the depository number CSD 53409, the names of the authors, and the literature citation.

Table III. Atomic coordinates and equivalent temperature-factors for the nonhydrogen-atoms of $K_2[S_2C=N-SO_2-C_6H_4-Cl] \cdot 2H_2O$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
K1	0.3909(1)	0.7286(1)	0.3368(1)	0.0383(14)
K2	0.4717(1)	0.1470(1)	0.2695(2)	0.0427(14)
S1	0.3775(1)	0.6442(2)	0.8360(2)	0.0474(15)
S2	0.4584(1)	0.4950(2)	0.6600(2)	0.0435(15)
S3	0.3725(1)	0.2516(1)	0.0835(2)	0.0336(14)
Cl	0.2108(1)	0.1576(2)	0.5107(2)	0.0405(18)
C1	0.9138(1)	0.0311(5)	0.8225(6)	0.0266(36)
N	0.9118(1)	0.1954(4)	0.9287(5)	0.0285(34)
O1	0.8644(1)	0.1171(4)	0.2546(4)	0.0466(33)
O2	0.8823(1)	0.4349(4)	0.1571(5)	0.0304(34)
C21	0.8271(1)	0.2647(3)	0.9225(3)	0.0335(37)
C22	0.7876(1)	0.2126(3)	0.0033(3)	0.0442(38)
C23	0.7512(1)	0.2357(3)	0.8772(3)	0.0465(40)
C24	0.7544(1)	0.3109(3)	0.6703(3)	0.0359(38)
C25	0.7940(1)	0.3630(3)	0.5895(3)	0.0466(38)
C26	0.8303(1)	0.3399(3)	0.7156(3)	0.0443(38)
OW1	0.5563(1)	0.0094(4)	0.3399(4)	0.0498(34)
OW2	0.5270(1)	0.2209(4)	0.8786(5)	0.0416(34)

Discussion

Although at first sight the crystal data of $K_2\mathbf{1} \cdot 2H_2O$ and $K_2\mathbf{2} \cdot 2H_2O$ look very similar, atomic coordinates do not reveal a close relationship. The relation becomes obvious by transforming the space group of $K_2\mathbf{2} \cdot 2H_2O$ from second to first setting, *i. e.* $P12_1/a1 \rightarrow P112_1/a$ ($a' = 31.517(3)$, $b' = 6.196(1)$, $c' = 7.189(1)$ Å, $\gamma' = 90.10(1)^\circ$)*. In order to describe the symmetry-relation between $K_2\mathbf{1} \cdot 2H_2O$ and $K_2\mathbf{2} \cdot 2H_2O$ precisely and under a more common point of view, a group-subgroup formalism is given [11]:

$$\begin{array}{c} Pnaa \\ \swarrow \quad \searrow \\ t2 \quad t2 \\ P12_1/a1 \leftarrow \not\leftrightarrow P112_1/a \end{array}$$

Although both hettotype space groups are subgroups of $Pnaa$ until now no aristotype compound has been observed**.

* The atomic coordinates of $K_2\mathbf{2} \cdot 2H_2O$ given in Table III refer to space group $P12_1/a1$ and are to be transformed by applying the matrix $\begin{bmatrix} 100 \\ 001 \\ 010 \end{bmatrix}$ and the origin shift vector $[00.50]$.

** The compound $K_2\mathbf{3} \cdot 2H_2O$ is isotype with $K_2\mathbf{1} \cdot 2H_2O$ and crystallizes monoclinically, space group $P12_1/a1$ with $a = 32.304(5)$, $b = 6.167(3)$, $c = 7.194(3)$ Å and $\beta = 92.39(6)^\circ$.

Molecular geometry of **1** and **2**

The structures of **1** and **2** are depicted in Fig. 1 and 2. Table IV contains significant interatomic distances and angles. Atoms S1, S2, C1, N, S3 and O2 in Fig. 1 form a planar arrangement (average deviations from least squares planes: 0.011 Å in **1** and 0.009 Å in **2**).

A plane containing the phenyl ring, S3 and Cl of **2** is shown in Fig. 2. The distances from O1 to these planes are 0.405 Å (**1**) and 0.411 Å (**2**). According to Koch and Moffitt [12] such a conformation of compounds containing SO_2 groups can be described as “case I of conjugation” referring to the π -system of the phenyl ring and the lone-pair located on N_{sp^2} while the π -system of the S_2CN moiety is of “case II”. The case I-type should favour strong conjugation with weakened oxy-sulphur bonds [12]. In **1** the S3–O2 bond is significantly elongated, while in **2** the elongation is not very pronounced.

Distances for S–O in the range of 1.43–1.46 Å are usually observed in SO_2 containing molecules [13–15]. The average bond length for S3–C21 in **1** and **2** (1.745 Å) is in agreement with the theoretical $S(VI)-S_{sp^2}$ value of 1.75 Å calculated from atomic radii and electronegativities and with experimental data obtained for sulphonylamides [16, 17]. The S3–N bond lengths in **1** and **2** (1.623 and 1.614 Å, respectively) show that the molecules contain S–N bonds of intermediate π -bond orders.

The bond lengths and angles in the S_2CN groups of **1** and **2** are quite similar and show the expected mesomeric charge distribution. The repulsive inter-

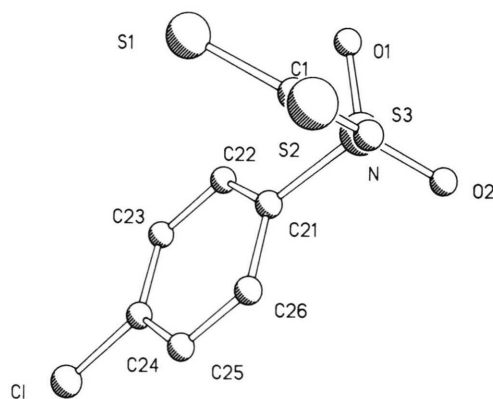


Fig. 1. Projection of **2** along the N–S3 bond. It can be seen that the $S_2C=N-SO$ framework is a planar arrangement.

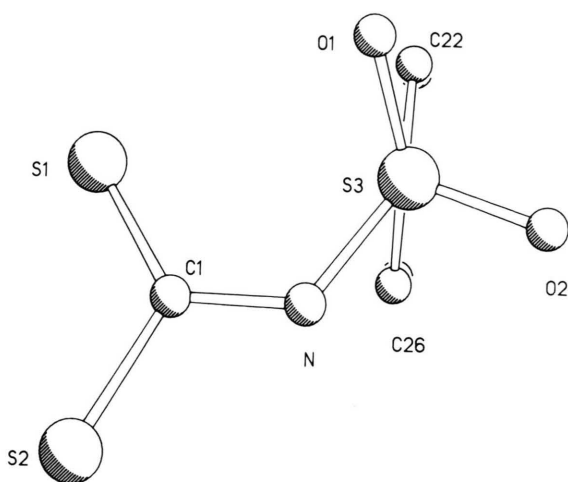


Fig. 2. Projection of **1** along the S3–C21 bond. The atoms of the phenyl ring together with S3 constitute a planar system while O1 is slightly tilted. In **2** Cl is also located in this plane.

action between S2 and the lone-pair located on N results in an elongation of the S2–C1 bond while the repulsive interaction between S1 and S3 is minimized by an increased bond angle S1–C1–N (see Table IV).

Table IV. Selected distances and angles in the anions **1** and **2** in Å and degrees with standard deviations in parenthesis.

	1	2
S1...S2	2.975(4)	2.975(1)
S1–C1	1.701(7)	1.704(4)
S2–C1	1.745(7)	1.741(3)
C1–N	1.342(9)	1.354(5)
N–S3	1.623(7)	1.614(3)
S3–O1	1.438(5)	1.443(3)
S3–O2	1.444(6)	1.449(3)
S3–C21	1.743(4)	1.747(3)
Cl–C24	–	1.707(3)
S1–C1–S2	119.4(4)	119.4(2)
S1–C1–N	126.7(5)	126.1(3)
S2–C1–N	113.9(5)	114.4(3)
C1–N–S3	122.1(5)	122.1(3)
N–S3–C21	108.7(3)	108.5(2)
N–S3–O1	113.8(3)	114.8(2)
N–S3–O2	103.8(4)	104.0(2)
O1–S3–O2	114.6(3)	114.3(2)
N–S3–C21–C26	38.6(2)	37.2(2)
Angle between planes*	81.5(5)	98.2(6)

* The least-squares planes in **1** and **2** are defined through the atoms S1, S2, C1, N, S3, O2 and S3–Ph with Cl in **2**.

Table V. Distances within the coordination polyhedra of potassium in $K_2\mathbf{1} \cdot 2H_2O$ and $K_2\mathbf{2} \cdot 2H_2O$ in Å.

	$K_2\mathbf{1} \cdot 2H_2O$	$K_2\mathbf{2} \cdot 2H_2O$
K1–O1	2.665(5)	2.671(3)
–O2	2.668(5)	2.677(3)
–OW2	2.888(6)	2.936(3)
–OW1	3.147(6)	3.212(4)
–S1	3.192(3)	3.181(1)
–S2	3.222(3)	3.189(1)
–S2	3.325(3)	3.368(1)
–Cl	–	3.382(5)
K2–OW2	2.821(5)	2.800(3)
–OW2	2.997(6)	3.033(3)
–OW1	2.823(6)	2.812(3)
–OW1	2.894(7)	2.876(3)
–O2	2.965(7)	2.960(3)
–N1	3.076(7)	3.048(3)
–S2	3.419(3)	3.415(1)
–S2	3.488(3)	3.506(2)

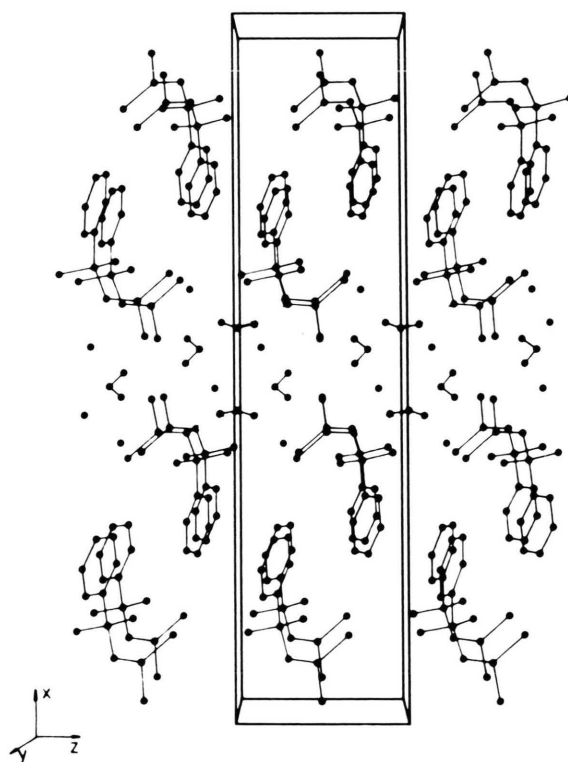


Fig. 3. Projection of the unit cell of $K_2\mathbf{1} \cdot 2H_2O$. The potassium ions are interspersed in the packing of **1**. $K_2\mathbf{2} \cdot 2H_2O$ adopts a similar packing.

Coordination of the K^+ ions

Fig. 3 shows the unit cell of $K_2\mathbf{1}\cdot 2H_2O$; that of $K_2\mathbf{2}\cdot 2H_2O$ looks rather similar when the space group setting is $P112_1/a$ with corresponding metric and positional parameters (see above).

The potassium ions K1 and K2 are interspersed in the packing of anions and exhibit irregular seven and eightfold coordination in $K_2\mathbf{1}\cdot 2H_2O$, while in $K_2\mathbf{2}\cdot 2H_2O$ the K1 ion has one additional contact with Cl from $\mathbf{2}$.

K1 is situated between anions $\mathbf{1}$ ($\mathbf{2}$) and forms unusually short contacts to O1 as well as to O2 of a sulfonyl group [18].

In each compound there is only one distance significant for hydrogen bonding involving the S2 atoms of $\mathbf{1}$ and $\mathbf{2}$. The values of 3.195(6) Å for OW2–S2 ($\mathbf{1}$) and 3.222(3) Å for OW2–S2 ($\mathbf{2}$) are relatively short. Hydrogen bonding to S2 is expected to be more likely than involving the S1 atom because the increased distance C1–S2 should result in more ionic character of S2 [19, 20].

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