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Carbonates, Thiocarbonates, and the Corresponding Monoalkyl Derivatives. 2. X-ray Crystal Structure of Potassium Methyltrithiocarbonate (KS_2CSCH_3)

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This study presents the first crystal structure determination of a potassium *S*-alkylthiocarbonate, the title compound potassium methyltrithiocarbonate (KS_2CSCH_3) Single crystals of KS_2CSCH_3 were obtained by the slow introduction of methylene chloride into a saturated solution of KS_2CSCH_3 in a 1:1 mixture of methylene chloride and tetrahydrofuran at 0 °C in a dry N_2 atmosphere. The compound crystallizes in the monoclinic space group $P2_1/c$ containing $Z = 4$ K^+ cations and $S_2CSCH_3^-$ anions per unit cell. The unit cell dimensions are $a = 7.6639(3)$ Å, $b = 6.5804(2)$ Å, $c = 12.8426(5)$ Å, and $\beta = 91.565(2)°$. The isomorphism to the structurally closely related compounds KO_2COCH_3, $KOSCOCH_3$, and KS_2COCH_3 is examined.

Introduction

In connection with an ongoing study of the orientations of ^{13}C NMR chemical shift tensors in potassium carbonates, thiocarbonates, and corresponding methyl derivatives, the knowledge of the crystal structures of the compounds is important. A new procedure to obtain single crystals of potassium methyltrithiocarbonate (KS_2CSCH_3) was developed. Potassium alkylcarbonates and *O*-alkylthiocarbonates (KO_2COR, KOSCOR, KS_2COR, with R = alkyl group) have been studied in great detail, and the X-ray structures of several members of this series with different alkyl groups are reported in the literature. Conversely, the structures of the *S*-alkylthiocarbonates (KO_2CSR, KOSCSR, KS_2CSR, with R = alkyl group) have not been reported. This is partly due to the instability of the two members of the series, KS_2COR and KOSCSR. The preparation and characterization of these two compounds as methyl derivatives were reported only recently.[1] This study presents the first crystal structure determination of a potassium *S*-alkylthiocarbonate, the title compound KS_2CSCH_3. The crystal data obtained for the material reveal that KS_2CSCH_3 is not isomorphous to the structurally closely related potassium alkylcarbonates and *O*-alkylthiocarbonates KO_2COCH_3, $KOSCOCH_3$, and KS_2COCH_3.

Experimental Section

Preparation of Single Crystals. Potassium methyltrithiocarbonate (KS_2CSCH_3) was prepared and characterized as previously described by Stueber et al.[1] Crystals of the material suitable for an X-ray diffraction analysis were grown by the slow introduction of methylene chloride into a saturated solution of the title compound in a 1:1 mixture of methylene chloride and tetrahydrofuran at 0 °C in a dry N_2 atmosphere. Both solvents were purchased from Aldrich as spectrophotometric grade materials and dried over molecular sieves before use. The crystals were separated by filtration, washed with methylene chloride, and dried in a vacuum over P_2O_5 at 30 °C for 3 days.

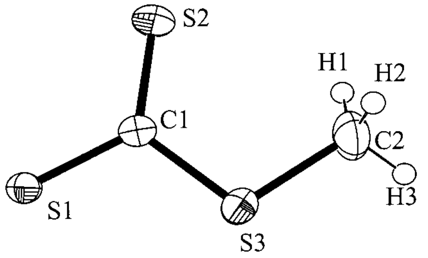

Figure 1. Atom numbering scheme and 20% thermal ellipsoids for the molecular $S_2CSCH_3^-$ anion.

X-ray Structure Determination. A yellow, plate-shaped crystal, 0.3 mm × 0.28 mm × 0.03 mm in size, was mounted on a glass fiber tip with tiny traces of viscous oil and then transferred to a Nonius KappaCCD diffractometer equipped with a Mo Kα radiation source ($\lambda = 0.710\ 73$ Å). Ten frames of data were collected at 200(1) K with an oscillation range of 1°/frame and an exposure time of 20 s/frame.[2] Indexing and unit cell refinement based on all observed reflections from those 10 frames indicated a monoclinic *P* lattice. A total of 3578 reflections ($\Theta_{max} = 32.71°$) were indexed, integrated, and corrected for Lorentz, polarization, and absorption effects using DENZO-SMN and Multi-Scan.[3] Postrefinement of the unit cell gave $a = 7.6639(3)$ Å, $b = 6.5804(2)$ Å, $c = 12.8426(5)$ Å, and $V = 647.43(4)$ Å^3. Axial photographs and systematic absences were consistent with the compound having crystallized in the monoclinic space group $P2_1/c$.

The structure was solved by a combination of direct methods and heavy atom using SIR97.[4] All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were located and refined isotropically using SHELXL97.[5] The weighing scheme $w = 1/[\sigma^2(F_o^2) + (0.0137P)^2 + 0.185P]$, where $P = (F_0^2 + 2F_c^2)/3$, was employed. The refinement converged to R1 = 0.0295, wR2 = 0.0634, and $S = 1.04$ for 1807 reflections with $I > 2\ \sigma(I)$ and to R1 = 0.0433, wR2 = 0.0695, and $S = 1.04$ for 2278 unique reflections and 67 parameters.[6] The maximum Δ/σ in the final cycle of the least squares was 0.003, and the residual peaks on the final difference Fourier map ranged from −0.352 to 0.330 e/Å^3. Scattering factors were taken from the International Tables of Crystallography, Volume C.[7,8]

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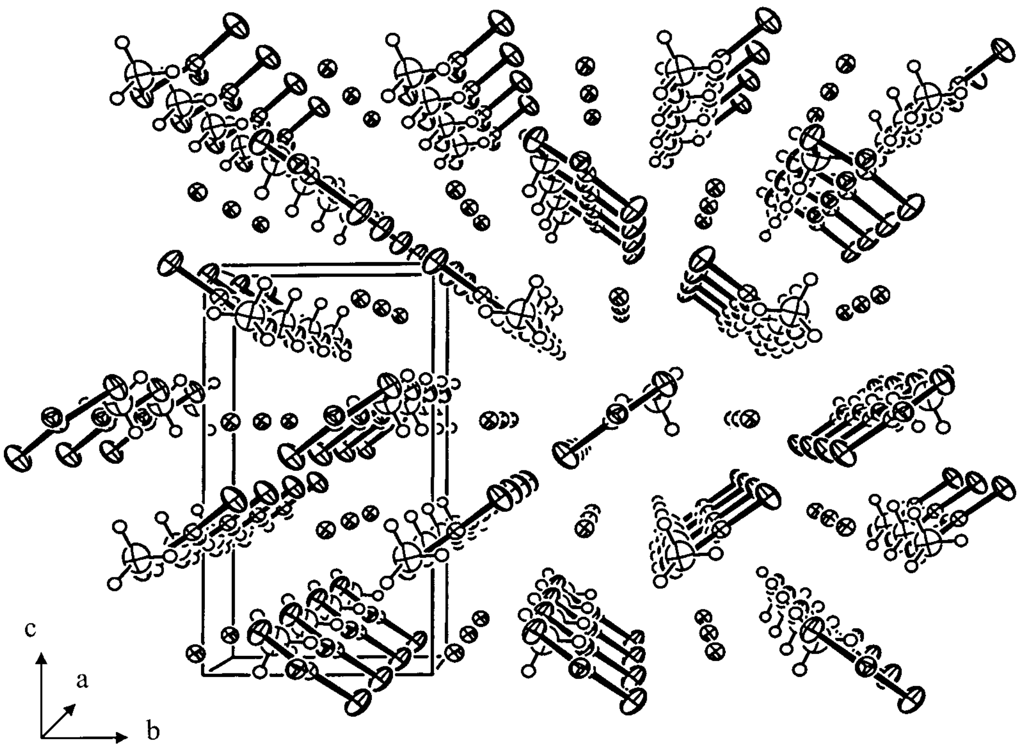

Figure 2. View of the crystal lattice along the crystallographic *a* dimension.

Table 1. Selected Crystallographic Data and Structure Refinement for KS_2CSCH_3

empirical formula	$C_2H_3KS_3$	ρ(calcd), mg/m^3	1.665
fw, g/mol	162.32	Z	4
λ, Å	0.710 73	a, Å	7.6639(3)
μ, mm^{-1}	1.650	b, Å	6.5804(2)
temp, K	200(1)	c, Å	12.8426(5)
cryst syst	monoclinic	β, deg	91.565(2)
space group	$P2_1/c$	R1^a [$I > 2\,\sigma(I)$, all]	0.0295, 0.0433
V, Å^3	647.43(4)	wR2^b [$I > 2\,\sigma(I)$, all]	0.0634, 0.0695

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

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for SHELXL^a

	x	y	z	U_{eq}
K	4984(1)	−3159(1)	3827(1)	32(1)
S1	4866(1)	1842(1)	3704(1)	23(1)
S2	8196(1)	3726(1)	4541(1)	39(1)
S3	8129(1)	147(1)	3101(1)	34(1)
C1	7087(2)	2015(2)	3838(1)	22(1)
C2	10433(2)	428(4)	3373(2)	45(1)

^{a} U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg)

bond distances		bond angles		dihedral angles	
S1−C1	1.7100(15)	C1−S3−C2	106.36(9)	S2−C1−S3−C2	4.28(13)
S2−C1	1.6624(14)	S2−C1−S1	126.33(9)	C1−S3−C2−H1	320.7
S3−C1	1.7562(14)	S2−C1−S3	122.23(9)	C1−S3−C2−H2	78.3
S3−C2	1.800(2)	S1−C1−S3	111.43(8)	C1−S3−C2−H3	194.8

Results and Discussion

The crystallographic data are summarized in Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times$ 10^3) are given in Table 2. The crystal is composed of potassium cations and molecular $S_2CSCH_3^-$ anions with four ion pairs per unit cell. Selected bond distances, bond angles, and dihedral angles in the $S_2CSCH_3^-$ anion are given in Table 3. Figure 1 introduces the corresponding atom numbering scheme and shows the 20% thermal ellipsoids. It was found that the S_2CS entity of the anion is essentially planar, with the methyl carbon rotated approximately 4−5° out of that plane (see dihedral angle S2−C1−S3−C2 in Table 3). Figure 2 shows a view of the crystal lattice along the crystallographic *a* dimension. The crystal consists of chains of anions along the crystallographic *a* direction that are rotated out of the *ac* plane. The anions are separated by the unit cell length in that dimension, 7.664 Å. In each chain, the methyl groups point in the same direction. Furthermore, the chains are staked along the crystallographic *b* dimension, separated by the unit cell length of that dimension, 6.580 Å, with alternating methyl group orientations and rotation angles from the *ac* plane. Alternating stacks are shifted relative to each other in the *b* and *a* dimensions. The distance between every other stack along the *c* dimension with the same methyl group orientation and angle to the *ac* plane is the length of the unit cell *c* dimension, 12.843 Å. The potassium cations are placed in rows along the crystallographic *a* dimension in the tunnels formed by the anion chains, separated by the unit cell *a* length. The resulting coordination polyhedron of the cations is illustrated in Figure 3. Each cation is surrounded by four $S_2CSCH_3^-$ anions

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(6) $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR2 = [\sum(w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$, and S = goodness-of-fit on $F^2 = [\sum(w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

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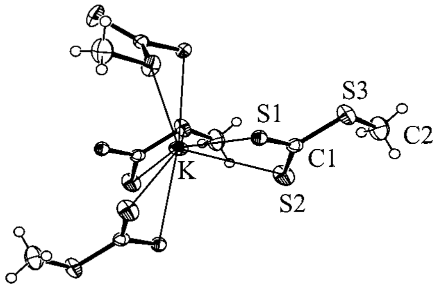

Figure 3. Coordination polyhedron of the potassium cations.

and interacts with four S1, two S2, and two S3 atoms. All eight K−S distances are similar, varying between 3.279 and 3.570 Å.

Comparing the structure of KS_2CSCH_3 to those structures found for the closely related potassium alkylcarbonates and *O*-alkylthiocarbonates KO_2COCH_3,[9] $KOSCOCH_3$,[10] and KS_2COCH_3[11] reveals that the crystals are not isomorphous.[12] KS_2CSCH_3 and $KOSCOCH_3$ both crystallize in a monoclinic space group with four ion pairs per unit cell and have similar unit cell dimensions;[13] however, the arrangement of the ions in the crystal lattice is completely different. KO_2COCH_3 and KS_2COCH_3 crystallize in a triclinic space group with two and six ion pairs per unit cell, respectively, and reveal very different unit cell dimensions and ion stacking arrangements. These findings are in agreement with the general observation that isomorphism is seldom found for crystals with small molecules and unit cells because variation in the identity of one atom causes a significant change in the structure.[14]

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Supporting Information Available: An X-ray crystallographic file in CIF format for KS_2CSCH_3 includes the complete data collection information, atomic coordinates, displacement parameters, and tables of bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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