On reactions of carbon disulfide induced by "naked" fluoride Part 3. Cyclization of carbon disulfide [1]

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Abstract

The tetramethylammonium salt of trithiocarbonic acid 3,5-dithione-1,2-dithiol-4-yl (1) is formed upon reaction of CS_2 with tetramethylammonium fluoride (TMAF) in dimethylformamide (DMF), probably via intermediate formation of FCS_2^-. The crystal structure of 1 was determined by X-ray structural analysis. © 1997 Elsevier Science S.A.

1. Introduction

Carbon disulfide reacts readily with "naked" fluoride to produce dithiofluoroformiate [1], and several reactions of CS_2 induced by "naked" fluoride can be best explained assuming at least an intermediate formation of FCS_2^- [2,3], but the crystal structure of the latter is hitherto unknown. Attempts to grow crystals from a reaction mixture of TMAF and CS_2 in DMF yielded unexpectedly the tetramethylammonium salt of trithiocarbonic acid 3,5-dithione-1,2-dithiol-4-yl monoester (1).

2. Results and discussion

Reactions of CS_2 and TMAF with fluoroaromatic compounds, which proceed via FCS_2^- formation [2], succeed best in DMF. Therefore, attempts were undertaken to grow single crystals suitable for structural investigations of $Me_4N^+ FCS_2^-$ in the solvent DMF as well. When TMAF was reacted with CS_2 in DMF, the two phase system became deep red upon heating if small amounts of water were present. Prolonged heating of the mixture up to 80 to 105 °C for about 3 weeks, followed by about 4 weeks at room temperature resulted in the formation of small, red, intensively refracting crystals which were stable in air. X-ray structural analysis revealed that a derivative of 1,2-dithiole-3-thione-4,5-dithiol-

ate had been obtained, i.e. the tetramethylammonium salt of its trithiocarbonic acid monoester (1). The salt crystallizes together with tetramethylammonium hydrogen difluoride in an orthorhombic unit cell, space group Pmnb (Table 1),

Table 1
Crystal data and structure refinement for 1

Identification code	tmcs
Empirical formula	C5 H12 F N S2
Formula weight	169.28
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	orthorhombic
Space group	Pmnb
Unit cell dimensions	$a = 14.615(5)$ Å $\alpha = 90°$
	$b = 14.663(5)$ Å $\beta = 90°$
	$c = 12.871(7)$ $\gamma = 90°$
Volume	2758(2) Å^3
Z	16
Density (calculated)	1.631 Mg m^{-3}
Absorption coefficient	0.696 mm^{-1}
$F(000)$	1440
Crystal size	$0.5 \times 0.3 \times 0.3$ mm^3
Theta range for data collection	2.11–25.04°
Index ranges	$-17 \leq h \leq 0$, $-17 \leq k \leq 0$, $0 \leq l \leq 15$
Reflections collected	2541
Independent reflections	2541 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2540/0/180
Goodness-of-fit on F^2	1.031
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0710$, $\omega R_2 = 0.1761$
R indices (all data)	$R_1 = 0.1208$, $\omega R_2 = 0.2104$
Extinction coefficient	0.0000(9)
Largest diff. peak and hole	0.571 and -0.415 e Å^{-3}

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which contains four dianions **1**, 16 tetramethylammonium cations and eight hydrogen difluoride anions. The structure could be well refined, with the exception of one of the tetramethylammonium cations together with its symmetry generated counterpart, where too much electron density was found around the nitrogen atom. One H atom is located on the crystallographic mirror plane between the F atoms of the HF_2^- ion.

The formation of the dianion **1** can be rationalized by a reaction sequence, as shown in Scheme 1. The first step in Scheme 1, i.e. the reduction of CS_2 is a well-known convenient way to the 4,5-dimercapto-1,3-dithiole-2-thione dianion (**2**) and further to other species based on the 1,3-dithiole ring system [4–12,14,15]. Both electrochemical reduction [4,5,7–9,11] and reduction with alkali metal [5,6,10,11, 14,15] have been successfully employed, and the solvent used was mostly DMF. In the reaction described here, there
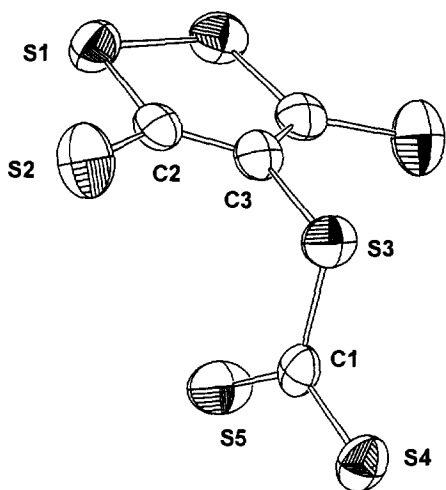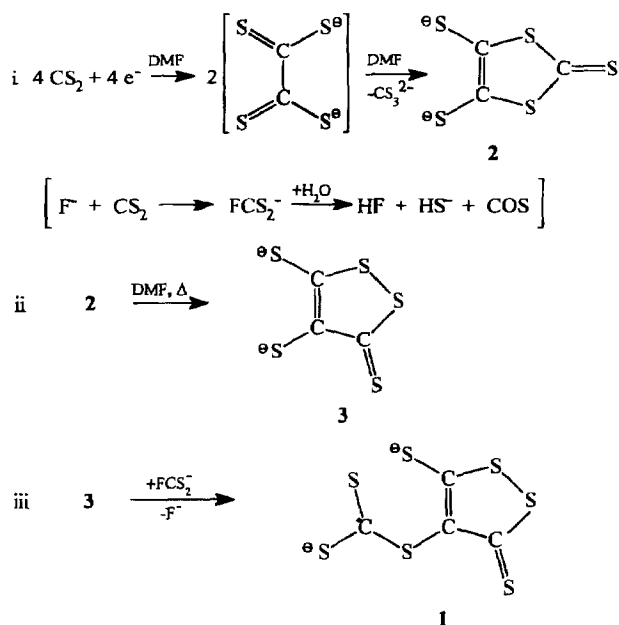
was no reducing agent added, only sulfide ions formed upon hydrolysis of FCS_2^- might have act as reducing agent. This way, the necessity of some water for the reaction finds its explanation. The second step in Scheme 1 is a rearrangement reaction of the 1,3-dithiole **2** to the 4,5-dimercapto-1,2-dithiole-3-thione dianion **3**, as it is reported to occur quantitatively when **2** is heated in DMF at 120–140 °C for 1–2 h [10–12]. The last step can be formulated as a reaction of dithiofluoroformiate with the tetramethylammonium salt of **3** (in analogy to the reaction of disodium 1,3-dithiole-2-thione-4,5-dithiolate with thiocarbonylchloride [7]).

1 is the largest inorganic carbon sulfide structural characterized [15] (Fig. 1). The symmetry of **1** is C_s, the atoms of the ring and S2, S2*, S3 are in one plane, and S3, C1, S4, S5 are in another one perpendicular to the former. Bond angles and distances of the heterocycle (Table 3) are in good agreement with those reported for the Ni(II) bis-complex of 1,2-

Scheme 1.

Fig. 1. ORTEP drawing of the molecular structure of **1**.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**. $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	$U(\text{eq})$
S(1)	3208(1)	6022(1)	1456(1)	50(1)
S(3)	2500	3497(1)	2991(2)	48(1)
S(4)	2500	2873(1)	5083(2)	50(1)
S(2)	4406(1)	4636(1)	2275(2)	68(1)
S(5)	2500	4890(2)	4684(2)	62(1)
N(1)	315(3)	7079(3)	4369(4)	47(1)
C(1)	2500	3812(5)	4325(6)	38(2)
C(2)	3329(4)	4963(4)	2061(4)	40(1)
C(3)	2500	4541(5)	2321(6)	41(2)
C(12)	1302(5)	7166(6)	4131(7)	68(2)
C(11)	36(6)	7864(6)	5024(7)	71(2)
C(14)	−200(6)	7102(6)	3375(6)	75(2)
C(13)	153(8)	6208(6)	4920(9)	91(3)
N(2)	7500	5079(5)	1688(6)	66(2)
F(2)	6752(4)	7669(5)	1619(4)	126(2)
C(21)	7500	4056(31)	1604(38)	171(6)
C(22)	8245(21)	5452(16)	2450(21)	171(6)
C(23)	7500	5626(21)	674(27)	171(6)
C(24)	8341(20)	5434(16)	1077(22)	171(6)
C(25)	6865(32)	4161(23)	1609(26)	171(6)
C(26)	7500	5439(26)	2779(34)	171(6)

Table 3

Bond lengths (Å) and angles (deg.) for **1**

S(1)–C(2)	1.747(6)
S(1)–S(1)#1	2.069(4)
S(3)–C(3)	1.756(8)
S(3)–C(1)	1.779(9)
S(4)–C(1)	1.686(8)
S(2)–C(2)	1.669(6)
S(5)–C(1)	1.647(8)
N(1)–C(12)	1.480(8)
N(1)–C(11)	1.484(8)
N(1)–C(14)	1.485(9)
N(1)–C(13)	1.480(9)
C(2)–C(3)	1.401(7)

(continued)

Table 3 (continued)

C(3)–C(2)#1	1.401(7)
C(12)–H(12A)	0.98(8)
C(12)–H(12B)	0.93(9)
C(12)–H(12C)	1.16(8)
C(11)–H(11A)	0.83(9)
C(11)–H(11B)	0.96(9)
C(11)–H(11C)	1.04(9)
C(14)–H(14A)	0.88(9)
C(14)–H(14B)	1.13(9)
C(14)–H(14C)	0.99(8)
C(13)–H(13A)	0.88(11)
C(13)–H(13B)	1.11(11)
C(13)–H(13C)	1.19(10)
N(2)–C(26)	1.50(4)
N(2)–C(21)	1.50(5)
N(2)–C(23)	1.53(3)
N(2)–C(24)#2	1.55(3)
N(2)–C(24)	1.55(3)
N(2)–C(22)	1.56(3)
N(2)–C(22)#2	1.56(3)
N(2)–C(25)	1.64(4)
N(2)–C(25)#2	1.64(4)
F(2)–HB	1.105(13)
C(21)–C(25)#2	0.94(5)
C(21)–C(25)	0.94(5)
C(22)–C(26)	1.17(3)
C(22)–C(24)	1.77(4)
C(23)–C(24)	1.36(3)
C(23)–C(24)#2	1.36(3)
C(25)–C(25)#2	1.86(9)
C(26)–C(22)#2	1.17(3)
C(2)–S(1)–S(1)#1	95.8(2)
C(3)–S(3)–C(1)	104.3(4)
C(12)–N(1)–C(11)	108.6(6)
C(12)–N(1)–C(14)	108.3(6)
C(11)–N(1)–C(14)	109.4(6)
C(12)–N(1)–C(13)	109.3(6)
C(11)–N(1)–C(13)	110.7(7)
C(14)–N(1)–C(13)	110.5(7)
S(5)–C(1)–S(4)	128.4(5)
S(5)–C(1)–S(3)	121.3(4)
S(4)–C(1)–S(3)	110.3(4)
C(3)–C(2)–S(2)	130.5(4)
C(3)–C(2)–S(1)	114.3(5)
S(2)–C(2)–S(1)	115.1(3)
C(2)#1–C(3)–C(2)	119.7(7)
C(2)#1–C(3)–S(3)	120.1(3)
C(2)–C(3)–S(3)	120.1(3)
N(1)–C(12)–H(12A)	114(5)
N(1)–C(12)–H(12B)	99(5)
H(12A)–C(12)–H(12B)	114(7)
N(1)–C(12)–H(12C)	119(4)
H(12A)–C(12)–H(12C)	106(6)
H(12B)–C(12)–H(12C)	106(7)
N(1)–C(11)–H(11A)	108(6)
N(1)–C(11)–H(11B)	116(5)
H(11A)–C(11)–H(11B)	115(8)
N(1)–C(11)–H(11C)	109(5)
H(11A)–C(11)–H(11C)	100(7)
H(11B)–C(11)–H(11C)	108(7)
N(1)–C(14)–H(14A)	107(6)
N(1)–C(14)–H(14B)	112(5)
H(14A)–C(14)–H(14B)	107(8)
N(1)–C(14)–H(14C)	120(5)

(continued)

Table 3 (continued)

H(14A)–C(14)–H(14C)	108(8)
H(14B)–C(14)–H(14C)	101(7)
N(1)–C(13)–H(13A)	110(7)
N(1)–C(13)–H(13B)	111(5)
H(13A)–C(13)–H(13B)	99(9)
N(1)–C(13)–H(13C)	115(5)
H(13A)–C(13)–H(13C)	116(8)
H(13B)–C(13)–H(13C)	104(8)
C(26)–N(2)–C(21)	115(3)
C(26)–N(1)–C(23)	128(2)
C(21)–N(2)–C(23)	117(2)
C(26)–N(2)–C(24)#2	110.9(13)
C(21)–N(2)–C(24)#2	107.4(14)
C(23)–N(2)–C(24)#2	52.5(11)
C(26)–N(2)–C(24)	110.9(13)
C(21)–N(2)–C(24)	107.4(14)
C(23)–N(2)–C(24)	52.5(11)
C(24)#2–N(2)–C(24)	105(2)
C(26)–N(2)–C(22)	44.7(11)
C(21)–N(2)–C(22)	113(2)
C(23)–N(2)–C(22)	110.6(13)
C(24)#2–N(2)–C(22)	138.9(14)
C(24)–N(2)–C(22)	69.5(14)
C(26)–N(2)–C(22)#2	44.7(11)
C(21)–N(2)–C(22)#2	113(2)
C(23)–N(2)–C(22)#2	110.6(13)
C(24)#2–N(2)–C(22)#2	69.5(14)
C(24)–N(2)–C(22)#2	138.9(14)
C(22)–N(2)–C(22)#2	88(2)
C(26)–N(2)–C(25)	110(2)
C(21)–N(2)–C(25)	35(2)
C(23)–N(2)–C(25)	112(2)
C(24)#2–N(2)–C(25)	78(2)
C(24)–N(2)–C(25)	134(2)
C(22)–N(2)–C(25)	136(2)
C(22)#2–N(2)–C(25)	86(2)
C(26)–N(2)–C(25)#2	110(2)
C(21)–N(2)–C(25)#2	35(2)
C(23)–N(2)–C(25)#2	112(2)
C(24)#2–N(2)–C(25)#2	134(2)
C(24)–N(2)–C(25)#2	78(2)
C(22)–N(2)–C(25)#2	86(2)
C(22)#2–N(2)–C(25)#2	136(2)
C(25)–N(2)–C(25)#2	69(3)
C(25)#2–C(21)–C(25)	161(9)
C(25)#2–C(21)–N(2)	81(4)
C(25)–C(21)–N(2)	81(4)
C(26)–C(22)–N(2)	65(3)
C(26)–C(22)–C(24)	116(4)
N(2)–C(22)–C(24)	54.9(13)
C(24)–C(23)–C(24)#2	129(4)
C(24)–C(23)–N(2)	64(2)
C(24)#2–C(23)–N(2)	64(2)
C(23)–C(24)–N(2)	63(2)
C(23)–C(24)–C(22)	108(3)
N(2)–C(24)–C(22)	55.7(13)
C(21)–C(25)–N(2)	65(4)
C(11)–C(25)–C(25)#2	9(4)
N(2)–C(25)–C(25)#2	56(2)
C(22)#2–C(26)–C(22)	138(5)
C(22)#2–C(26)–N(2)	71(3)
C(22)–C(26)–N(2)	71(3)

Symmetry transformations used to generate equivalent atoms: #1, $x + 1/2$, y, z; #2, $x + 3/2$, y, z.

Table 4

Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	61(1)	43(1)	46(1)	3(1)	5(1)	−9(1)
S(3)	71(2)	29(1)	45(1)	−1(1)	0	0
S(4)	51(1)	40(1)	58(1)	13(1)	0	0
S(2)	46(1)	63(1)	93(1)	−8(1)	−3(1)	5(1)
S(5)	103(2)	36(1)	47(1)	−3(1)	0	0
N(1)	40(3)	48(3)	54(3)	−4(2)	8(2)	1(2)
C(1)	24(4)	41(4)	49(5)	7(4)	0	0
C(2)	50(4)	37(3)	34(3)	−9(2)	−1(3)	−3(3)
C(3)	54(5)	29(4)	40(5)	−7(3)	0	0
C(12)	40(4)	92(6)	71(5)	0(4)	17(4)	−5(4)
C(11)	59(5)	75(5)	79(5)	−28(4)	6(4)	11(4)
C(14)	68(5)	96(6)	61(5)	−12(4)	−17(4)	11(5)
C(13)	86(7)	63(5)	125(8)	35(5)	28(6)	−1(5)
N(2)	103(7)	53(5)	42(4)	−9(4)	0	0
F(2)	98(4)	176(6)	102(4)	−5(4)	−24(4)	−16(4)

Table 5

Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**

	x	y	z	$U(\text{eq})$
H(12A)	1499(56)	6645(56)	3738(67)	102
H(12B)	1643(60)	7199(53)	4767(67)	102
H(12C)	1404(58)	7710(51)	3733(68)	102
H(11A)	−581(66)	7775(56)	5261(66)	107
H(11B)	69(63)	8415(60)	4623(68)	107
H(11C)	437(60)	7910(54)	5612(67)	107
H(14A)	−840(65)	7012(59)	3512(70)	112
H(14B)	18(63)	6626(57)	2927(71)	112
H(14C)	−113(65)	7682(57)	3045(69)	112
H(13A)	−491(77)	6136(66)	5046(82)	137
H(13B)	475(74)	6212(67)	5570(84)	137
H(13C)	369(74)	5711(68)	4500(82)	137
HB	7500	7704(53)	1498(65)	43(22)

dithiole-3-thione-4,5-dithiolate [10]. The planarity indicates that all carbon atoms are sp^2 hybridized, and the C–C distances are equal and rather short, these are facts which argue a delocalized π-electron system, as it was discussed in case of the 2-dimercaptomethylidene-4,5-dithione-1,3-dithiole dianion [15] as well as in case of the "pseudo-1,2-dithiolo-1,2-dithiole" [13]. The S2–C2 as well as the S5–C1 and the S4–C1 distances are about half way between those reported for the C=S double bond and C–S single bond (1.56 and 1.8 Å, respectively [13]). Thus, the situation at **1** might be best represented by three resonating structures.

3. Experimental details

The synthesis was performed as described above, using dry CS_2 and dry DMF and TMAF with about 0.5 mole H_2O per mole fluoride.

3.1. Crystal structure

Red crystals of **1** suitable for X-ray crystallography were obtained from the DMF solution. A crystal ($\sim 0.5 \times 0.3 \times 0.3$ mm^3) was mounted on a glass fibre. Data were collected on a Stoe 4-circle diffractometer using Mo Kα radiation, $\lambda = 0.71069$ Å. 2774 reflections were collected. Systematic absence indicated the space group Pmnb, No. 62. The structure was solved by direct methods ($\blacklozenge\square^{™}\blacklozenge \blacklozenge$86 [16]). Full matrix least-squares refinement based on F_o^2 ($\blacklozenge\square^{™}\blacklozenge \blacklozenge$93 [17]), anisotropic thermal parameters for C, N, F, S except for the carbon atoms at N2, 240 crystallographic independent reflections, and 1625 reflections with $F_o > 4\sigma(F_o)$. Molecular drawings were performed using ORTEP [18] as modified by Zsolnai [19]. One tetramethylammonium ion is severely disordered. The carbon atoms around N2 have been refined on several split atom positions to take account of the electron density around N2. Any C–N distance at N2 is meaningless. Important crystallographic details, bond length and angles are summarized in Tables 1–5.

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