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SYNTHESIS, STRUCTURE, AND REACTIONS OF THIOCARBONIC ACID DERIVATIVES NEW PENTATHIODIPERCARBONATES, $(RSS)_2C{=}S$, α,α,α-TRIS(DISULFIDES), AND THE FIRST α,α,α-TRIS(TRISULFIDE)

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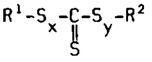
Abstract - Novel bis(perhaloalkyl) pentathiodipercarbonates 5b-d have been synthesized by reaction of sulfenyl chlorides with metal trithiocarbonates, and the heptathio analog 21a was prepared similarly. Lenthionine 19 is the main product when diiodomethane is treated with sodium tetrathiopercarbonate. A rearrangement of bis(alkyldithio)chloromethanesulfenyl chlorides 22 to alkyldithio)(alkyltrithio)dichloromethanes 24 has been observed. Additions of sulfenyl chlorides and of thiosulfenyl chlorides to the thiocarbonyl compounds 5 and 21a were achieved in acetonitrile. The structures of the first crystalline pentathiodipercarbonate 5a and α,α,α-tris(disulfide) 29a, and of the first reported α,α,α-tris(trisulfide) 31a have been determined by X-ray crystallography.

INTRODUCTION

A perhaloalkyl group as substituent R in *e.g.* classes of compounds with an oligosulfide substructure, $R\text{-}S_x\text{-}$, often has a stabilizing effect and may facilitate the isolation and handling of otherwise labile species. Thiocarbonic acid esters with the general formula 1 are uncommon, most of the literature concerning 1 being patents claiming syntheses and applications,[1] and for x > 1 only the trihalomethyl substituted compounds 2 (n = 0, [2,3] n = 1,[4] n = 2,[4] n = 3)[4-6] and 3[4] have with certainty been isolated and satisfactorily characterized. No compound 1 with x or y larger than 3 has been reported.



$$R^1\text{-}S_x\text{-}\underset{\underset{\displaystyle S}{\|}}{C}\text{-}S_y\text{-}R^2$$

1 x = 1, 2, 3
y = 2, 3

$(CCl_{3-n}F_nSS)_2C{=}S$

2 n = 0-3

$(CF_3SSS)_2C{=}S$

3

Whereas the pentathiodipercarbonate 5a (2, n = 0) in reactions with a number of nucleophiles is degraded, merely acting as a thiophosgene substitute,[2] we recently found [3,7] that new derivatives can be obtained from the reaction of electrophiles with the thiocarbonyl functionality of 5a.

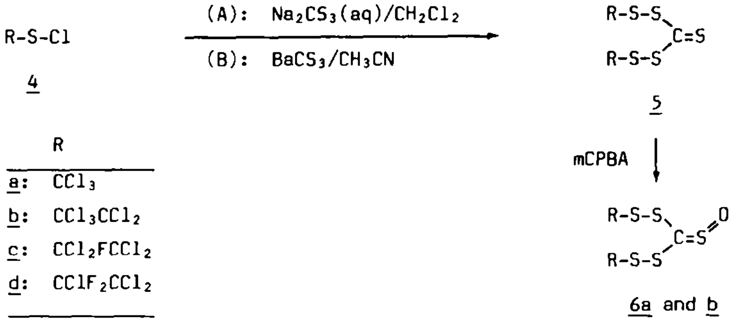
This paper describes an elaboration of similar reactions of novel pentathiodipercarbonates and related substances.

RESULTS AND DISCUSSION

Spectral and analytical data and yields of new compounds are summarized in Tables 1 and 2. Mass spectra are not given because in general no molecular peaks could be detected and only uncharacteristic fragmentation patterns of poor reproducibility appeared.

Reaction of Sulfenyl Chlorides and of Thiosulfenyl Chlorides* with Metal Trithiocarbonates

The new pentathiodipercarbonates 5b-d can be prepared by either of the two methods (A) and (B), eq. (1).



(1)

(2)

	R
a:	CCl_3
b:	CCl_3CCl_2
c:	CCl_2FCCl_2
d:	$CClF_2CCl_2$

throughout

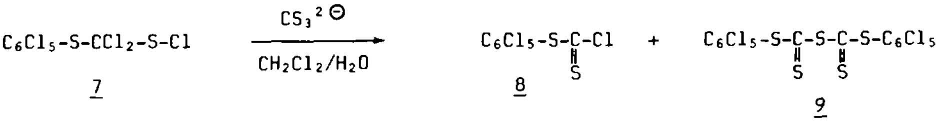
By method (A) excess of freshly prepared aqueous sodium trithiocarbonate is added to the sulfenyl chloride in an organic solvent according to Fischer and Gottfried.[2c,3]

We have examined an alternative method (B) making use of anhydrous barium trithiocarbonate in acetonitrile suspension. The barium salt is easily prepared and has a long shelf life.[8] The side reactions in acetonitrile of 4 and 5 (eq. (18)) may, if 5 rather than 29 is the desired product, be suppressed by excess barium trithiocarbonate.

The compounds 5a-c are orange crystalline solids, stable for years at -25 °C in the dark. Signals of low intensity (δ 218.1, 100.3 (J 30), and 121.8 (J 306) in the ^{13}C NMR spectrum of 5c can be ascribed to CCl_3CClF-SS-C(=S)- groups originating from $CCl_3CClFSCl$ present as an impurity in 4c. The analysis of crude 5d (an orange-red liquid), though not quite satisfactory, together with the spectral data leaves no doubt that 5d is the main product. No crystallization of 5d or purification by chromatography could be achieved.

Oxidation of 5b with m-chloroperbenzoic acid gave the expected sulfine 6b, cf. the oxidation of 5a[3] and 2 (n = 3).[5]

So far we have not been able to isolate pentathiodipercarbonates other than 5a-d. The reaction of the sulfenyl chloride 7 with sodium trithiocarbonate, eq. (3), gave the chlorodithioformate 8 and a product assigned the structure 9. Dechlorination of 7 by the trithiocarbonate dianion and further reaction of the resulting 8 with $CS_3^{2\ominus}$ as a source of $S^{2\ominus}$ may explain the formation of 9.



$$\underset{7}{C_6Cl_5\text{-S-}CCl_2\text{-S-Cl}} \xrightarrow[CH_2Cl_2/H_2O]{CS_3^{2\ominus}} \underset{8}{C_6Cl_5\text{-S-}\underset{\|}{\overset{}{C}}\text{-Cl}}\;\;+\;\; \underset{9}{C_6Cl_5\text{-S-}\underset{S}{\underset{\|}{C}}\text{-S-}\underset{S}{\underset{\|}{C}}\text{-S-}C_6Cl_5} \qquad (3)$$

Pentachlorobenzenesulfenyl chloride 10 yielded 92 % of the known[9] trisulfide 11 in its reaction with sodium trithiocarbonate. A yellow intermediate immediately precipitating and gradually loosing its color might have been $C_6Cl_5SSC(=S)S^{\ominus}$ or 5 (R = C_6Cl_5) decomposing by elimination of carbon disulfide.

$$\underset{10}{2\ C_6Cl_5\text{-S-Cl}} \;+\; CS_3^{2\ominus} \xrightarrow[-\ CS_2]{-\ 2\ Cl^{\ominus}} \underset{11}{C_6Cl_5\text{-S-S-S-}C_6Cl_5} \qquad (4)$$

p-Toluenesulfenyl chloride treated according to method (A) gave three products. The trisulfide 12 and a low yield of the trithiocarbonate 14 could be isolated by chromatography.

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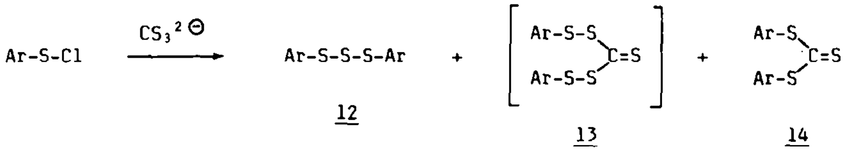
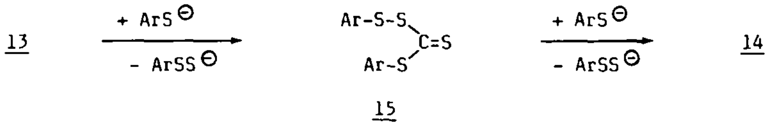
* "Thiosulfenyl chloride", though a misnomer, is a convenient and widely used synonym for chloro (organo)disulfane (organyl-S-S-Cl)


(5)

Ar = p-tolyl throughout

A yellow fraction contaminated with 12 contained a thiocarbonyl compound (different from 14 according to TLC) which presumably has been the pentathiodipercarbonate 13. The yellow compound decomposed upon attempted further chromatographic purification giving 12, but no 14, suggesting that 14 was formed during the reaction and not by spontaneous extrusion of sulfur from 13 during work-up. The loss of sulfur necessarily involved in the formation of 14 might take place by nucleophilic catalysis as proposed in eqs (6)-(8), where $Nu^{\ominus}$ is some unspecified nucleophile and Ar-S-X is e.g. 13.

$$Nu^{\ominus} + Ar\text{-}S\text{-}X \longrightarrow Nu\text{-}X + ArS^{\ominus} \qquad (6)$$


(7)

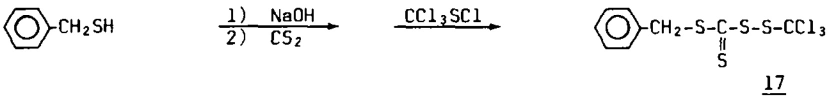
$$ArSS^{\ominus} \rightleftharpoons 1/8\ S_8 + ArS^{\ominus} \qquad (8)$$

The presence of a labile tetrathiopercarbonate 15 mixed with 13 in the impure yellow fraction cannot be ruled out. The phenyl analog of 15 has been reported [1d] but following a similar approach, eq. (9), we obtained only bis(p-tolyl) disulfide 16.

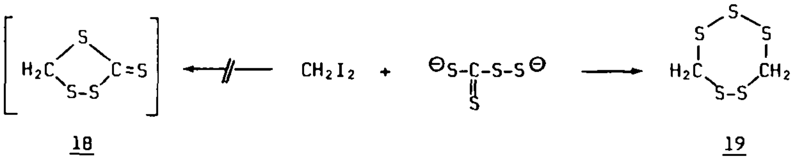
$$ArSH \xrightarrow[2)\ CS_2]{1)\ NaOH} \xrightarrow{+\ ArSCl} [15] \xrightarrow[-\ CS_2]{} \underset{16}{Ar\text{-}S\text{-}S\text{-}Ar} \qquad (9)$$

Whether an intrinsic instability of 15 (if formed at all) or the reaction conditions applied are responsible for the formation of 16 rather than 15 is unknown. Alkylation of metal tetrathiopercarbonates at elevated temperatures has been reported to give disulfides.[10]

A stable tetrathiopercarbonate 17 was prepared according to eq. (10).

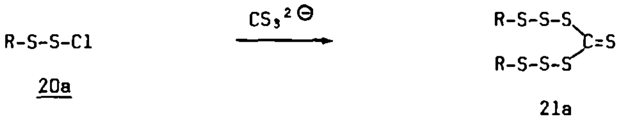

(10)

Cyclic tetrathiopercarbonates are unknown. Intending to study reactions of the thiocarbonyl functionality and prospective elimination of carbon disulfide we tried to synthesize 1,2,4-trithiolane-3-thione 18 from methylene halides and metal tetrathiopercarbonates,[11] but obtained instead varying amounts of 1,2,3,5,6-pentathiepane 19 (lenthionine, a naturally occurring compound)[12] and unidentified polymers.


(11)

In one case (see Experimental) lenthionine was obtained in a quite good yield compared with the best method in the literature.[12d]

Trichloromethylthiosulfenyl chloride 20a reacts with aqueous sodium trithiocarbonate to give 21a. The spectral data of the crude product (pure judging from TLC) are consistent with the structure 21a. The orange liquid 21a could not be brought to solidify and was not purified. In line with the reported [4] stability of 3 there is no indication that 21a should be unstable with respect to loss of carbon disulfide, specifically no decolorization upon standing has been observed.



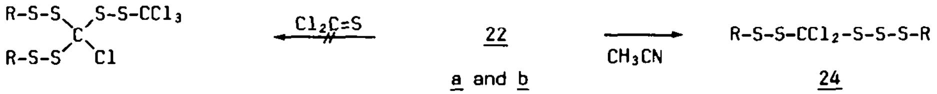
20a 21a (12)

Sulfenyl Chlorides from Chlorination of the Thiocarbonyl Compounds 5 and 17[13]

Chlorination of 5b and c can be carried out in the same way as the chlorination of 5a,[3] i.e. a titration of the orange 5 with a tetrachloromethane solution of chlorine to give the almost colorless 22. In pure form the sulfenyl chlorides are stable crystalline compounds.

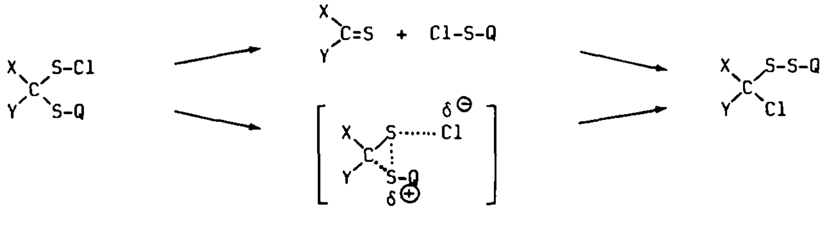
a, b, and c 22 (13)

In acetonitrile a decomposition of 22 takes place. Thus, attempts to prepare the tris(disulfides) 23a and b by addition of 22a and b, respectively, to thiophosgene in acetonitrile were unsuccessful, the only isolated products being the dichloro(alkyldithio)(alkyltrithio)methanes 24a and b which are also formed in the absence of thiophosgene when the sulfenyl chlorides are allowed to stand in acetonitrile at ambient temperature for some days, or in chloroform with HgCl$_2$ as a catalyst.



23 a and b 24 (14)

These are the first reported examples of migration of alkyldithio groups (Scheme 1, Q = RS) in a well precedented rearrangement of sulfenyl chlorides bearing organylthio groups in the α-position.[13] Elimination-addition mechanisms (X = Y = Q = Cl;[14] X = AlkO, Y = Q = Cl)[15] and transition states with more (X = CF$_3$S or F, Y = Cl, Q = CF$_3$)[16] or less (X = AlkO, Y = Cl, Q = Alk)[17] charge separation have been suggested.

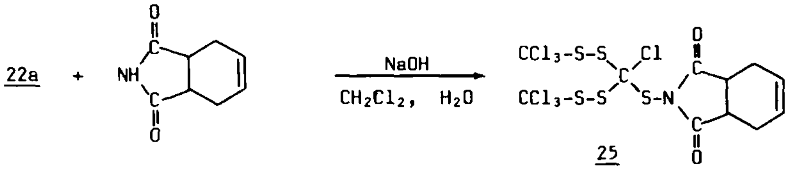


SCHEME 1

In our case a moderate yield of rearrangement product could be isolated and no other product was identified. The residue from the rearrangement of 22a after removal of 24a showed two IR absorptions in the C=S region at 1120 and 1080 cm^{-1}, tentatively ascribed to thiophosgene[18] or

$CCl_3SSC(=S)Cl$ [19] and 5a, respectively.

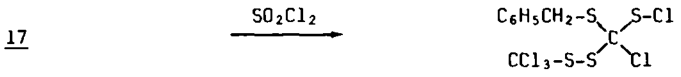
The reaction of 22a with tetrahydrophthalimide, eq. (15), gave the expected substitution product 25. Compound 25 may be considered as derived from the known fungicide captan [20] by replacement of two chlorine atoms by two trichloromethyldithio groups, but contrary to expectations no fungicidal activity has been found.



25

(15)

In contrast to the pentathiodipercarbonates 5a-d the tetrathiopercarbonate 17 is readily chlorinated with sulfuryl chloride. Pure 26 can be stored at room temperature for days without decomposition, but in chloroform a noticeable decay can be observed within the time it takes to prepare a sample for ^1H NMR and record the spectrum (see Experimental).

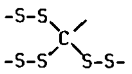


26

(16)

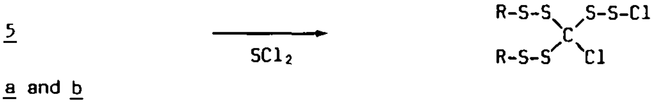
Reaction of 5 and of 21 with S-Cl bonds

Thione S-sulfenylation of 5 leads to compounds with the unusual α,α,α-tris(disulfide) substructure 27 which until recently [3] had one reported precedent (29, R = CF_3)[5] only.[21]



27

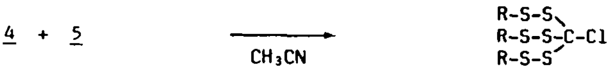
Previously[3] we have reported the addition reaction of sulfur dichloride with 5a. Similarly, 5b in excess sulfur dichloride at -25 °C in 18 hours gives a quantitative yield of the adduct 28b.



28

(17)

Unlike sulfur dichloride the sulfenyl chloride 4a reacts extremely slowly with 5a, even when 4a is used as solvent.[3] Also in contradistinction to this finding is the easy formation of 29 (R = CF_3) from Tl_2CS_3 and CF_3SCl.[5] However, if acetonitrile is used as reaction medium the reaction rate is dramatically enhanced.[3,22] The preliminarily reported [3] yield of 29a can be improved by prolonging the reaction time or by heating to reflux. The structure of the first [3] isolated 29a has been established by X-ray crystallography (see below) and the identity of the product from the direct synthesis, eq. (18), with the original sample follows from the spectral and analytical data in Tables 1 and 2. The new tris(disulfides) 29b and c can be prepared likewise.

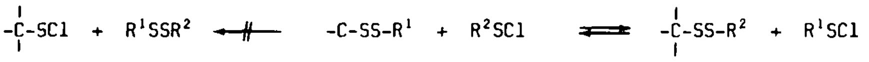


a, b, and c

29

(18)

In the reaction of an unsymmetrical disulfide with a sulfenyl chloride the new S-S bond is preferentially formed between the sulfenyl sulfur and the disulfide sulfur with the highest electron density.[23a] Accordingly, the S-S bond in 5 and/or 29 may react with 4.[23b] This was demonstrated in an attempt to synthesize an unsymmetrically substituted tris(disulfide) from the reaction of 4b and 5b in acetonitrile. After several days at room temperature a small amount of the symmetrically substituted tris(disulfide) 19b precipitated, indicating that a series of exchange reactions, eq. (19), had occurred.

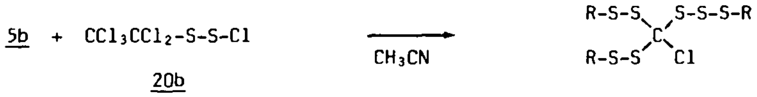


$$-\overset{|}{\underset{|}{C}}-SCl + R^1SSR^2 \nleftarrow -C-SS-R^1 + R^2SCl \rightleftharpoons -\overset{|}{\underset{|}{C}}-SS-R^2 + R^1SCl \qquad (19)$$

$R^1 = CCl_3$, $R^2 = CCl_3CCl_2$

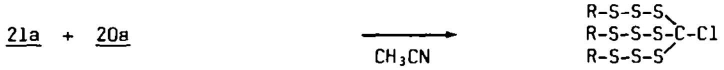
It is likely that all four possible tris(disulfides) have been present in the mixture and that 29b precipitated simply because of a relatively low solubility.

The components of the mixture from the reaction of 5b with pentachloroethylthiosulfenyl chloride 20b proved difficult to separate, but a minute amount of analytically pure adduct 30b could be obtained.



30b (20)

If the reaction of the thiosulfenyl chloride 20a with trithiocarbonate dianions is carried out according to method (B) the orange color of initially formed 21a gradually fades away and only colorless crystals can be isolated. Ambiguous analytical and spectroscopic data of this dimorphous substance called in question its identity until X-ray crystallography finally established the α,α,α-tris(trisulfide) structure 31a.



31a (21)

Authentic 21a prepared according to eq. (12) also gives a low yield of 31a in reaction with 20a in acetonitrile.

Neither the tetrathiopercarbonate 17 nor the trithiocarbonate S,S-dioxide[24] $4\text{-}CH_3C_6H_4SO_2\text{-}C(=S)\text{-}SC_6H_5$ reacts with trichloromethansulfenyl chloride in acetonitrile.

X-Ray Structure Determinations

The structures of 5a, 29a and 31a were confirmed by X-ray diffraction. Crystals of bis(trichloromethyl) pentathiodipercarbonate 5a, $C_3Cl_6S_5$, are monoclinic, $P2_1/a$, with a = 23.054(13), b = 10.468(6), c = 5.895(3) Å, β = 105.29(3)°, Z = 4. Chlorotris(trichloromethyldithio)methane 29a, $C_4Cl_{10}S_6$, is monoclinic, $P2_1/n$, a = 19.522(4), b = 5.963(1), c = 17.149(3) Å, β = 103.43(1)°, Z = 4. Crystals of chlorotris(trichloromethyltrithio)methane 31a, $C_4Cl_{10}S_9$, are rhombohedral, R3c, a = 18.697(3), c = 11.460(2) Å, Z = 6.

The bond lengths, most angles and torsion angles for all three structures are collected in Table 3. Drawings of the molecular structures are given in Fig.1.

The pentathiodipercarbonate 5a has a localized C-S double bond; all other bonds have the lengths of typical single bonds. The tris(disulfide) 29a shows what influence packing forces can have on the geometry; whereas 31a has crystallographic threefold symmetry, one branch of 29a is twisted differently as seen from the torsion angles. The bond angles of this branch differ from the corresponding ones, and even the C-S and S-S bond lengths seem to differ; these changes are apparently necessary to avoid a too close intrachain S•••Cl contact.

TABLE 1

Comp.	Mp. °C (solvent), or n_D	^{13}C NMR ($CDCl_3$), * δ(J_{C-F} in Hz) or ^{1}H NMR ($CDCl_3$)δ	IR solids: KBr pellets liquids: films between NaCl plates			Yield. Purified (crude)	Procedures
5b	113-114 (CH_2Cl_2)	218.5 104.7 104.0	1080(s) 1040(w) 970(w) 865(vw) 838(m)	815(m) 790(s) 780(s) 743(s) 665(s)	530(vw) 470(w) 460(vw)	20-36 (73)	b)
5c	40-42 (acetone)	217.9 122.4(309) 99.5(30)	1100(s) 1080(s) 998(s) 900(m) 870(m)	855(m) 834(s) 810(s) 775(s) 756(s)	710(s) 530(w) 505(vw) 470(w)	46 (70-80)	b)
5d	n_D^{21} 1.5927	217.2 127.0(302) 93.9(33)	1150(s) 1080(s) 1010(s) 860(s) 850(s)	830(s) 810(s) 770(s) 758(s) 738(s)	620(m)	(67)	b)
6b	103-104 (acetone)	187.0 104.8 104.4 104.2	1120(s) 1010(w) 970(w) 915(w) 850(w)	830(w) 785(m) 770(s) 750(s) 740(s)	665(s) 535(vw) 450(vw)	49	Ref.3
9	dec.130 (benzene)	not available	1340(s) 1315(s) 1080(s) 880(w) 810(m)	760(m) 720(m) 690(s) 680(m) 600(w)		17	a) c)
17	67-69 (acetone)	220.1 98.8 133.4 42.7 129.1 128.6 127.9	1500(w) 1460(w) 1070(vs) 1030(m) 855(s)	840(m) 785(s) 760(s) 740(s) 705(s)	690(s) 570(w) 470(m)	53 (87)	c)
21a	n_D^{20} 1.6965	217.4 99.4	1100(w) 1080(s) 820(m) 790(vs) 770(vs)	740(vs)		(58)	a)
22b	85-87 (petroleum) ether/CH_2Cl_2 2:1)	105.3 103.3 95.4	970(w) 840(w) 810(w) 790(m) 775(s)	742(s) 660(m) 510(w)		97 (100)	Ref.3
22c	41-43 (petrolum ether)	122.6(308) 98.7(30) 95.0	1100(s) 1000(s) 902(w) 870(m) 845(m)	830(m) 815(m) 780(s) 760(s) 710(m)	685(m) 510(m) 440(vw) 425(vw)	(100)	Ref.3
24a	53-54 (acetone)	99.6 99.0 98.1	791(s) 785(s) 778(s) 760(s) 745(s)	730(s) 710(s) 475(w) 443(w) 437(w)		(57)	c)
24b	88-89 (acetone)	105.0 104.5 104.0 102.9 99.9	975(w) 880(w) 830(w) 783(m) 765(s)	750(s) 742(s) 730(m) 665(m) 477(w)	430(w) 420(w)	(54)	c)
25	118-122 (ether)	177.8 23.3 127.2 98.1 94.4 39.2	1740(vs) 1440(w) 1300(s) 1200(m) 1170(s)	980(m) 840(w) 795(s) 765(s) 742(s)	730(s) 700(m) 580(w)	51	c)

- continued -

Table 1 (continued)

26	49-50 (petroleum ether)	^{1}H NMR: 7.23 (s,5H) 4.13 (s,2H) c)	1500(m) 1480(w) 1440(w) 1100(s)§ 780(s)	765(s) 745(s) 690(s)		(98)	c)
28b	67-70 (petroleum ether/CH_2Cl_2 3:1)	105.3 103.3 97.3	962(w) 840(w) 790(m) 770(s) 741(s)	762(m) 758(m) 510(w) 475(w) 430(vw)		54 (83)	Ref.3
29a	78-79 (acetone)	98.4 93.5	832(m) 795(s) 785(s) 761(s) 758(s)	735(s) 725(s) 443(w)		49	c)
29b	148-149 (acetone)	105.5 103.5 95.8	960(w) 835(m) 810(m) 785(s) 770(s)	745(s) 660(m) 430(w)		56	c)
29c	77-79 (acetone)	122.7(308) 98.8(29) 95.1	1090(s) 998(s) 899(m) 870(m) 840(m)	825(m) 805(m) 780(s) 755(s) 715(m)	698(m) 682(m) 430(vw)	55	c)
30b	116-118 (acetone)	not available	832(w) 780(s) 741(s) 663(m) 480(vw)	485(vw) 420(vw)		4	c)
31a	81 125 130-140 (ether/CH_2Cl_2)	99.7 98.9 c)	780(s) 750(s) 735(s) 502(vw) 470(w)	443(w)		13	b) c)

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* Normalized to $\delta(CDCl_3)$ at 77.0 ppm

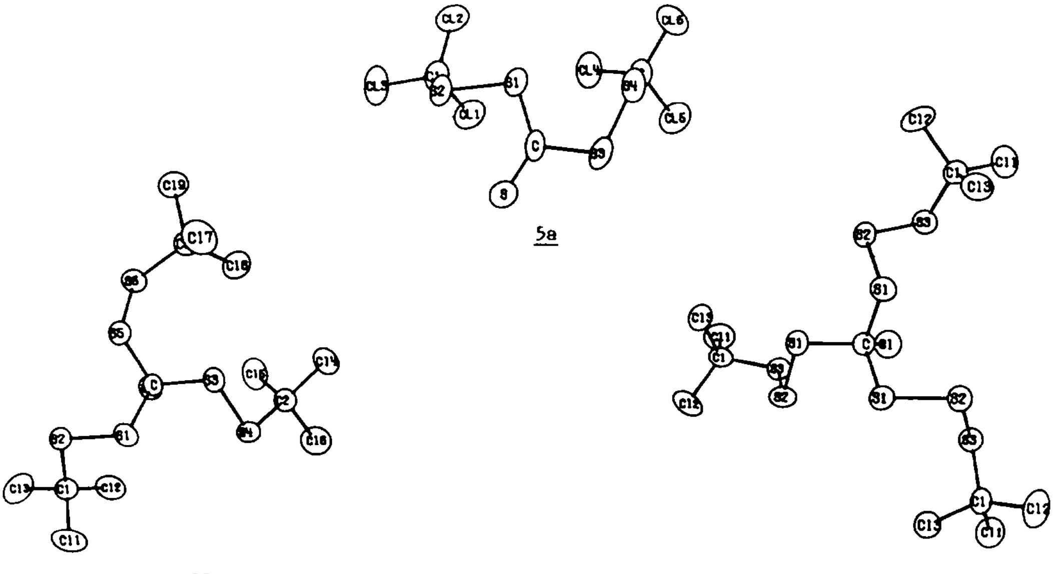
§ Absent in the spectrum of a freshly prepared solution of 26 in CH_2Cl_2

a) Prepared by method (A), eq.(1), cf. Ref.3

b) Prepared by method (B), see Experimental

c) See Experimental for more details.

FIGURE 1. Perspective drawings of the three molecules investigated, showing the numbering used



5a

29a

31a

TABLE 2. Analytical data, single determinations

Comp.	Formulae	(MW)	Found(calculated) in %				
			C	H	Cl	N	S
5b	$C_5Cl_{10}S_5$	(574.91)	10.66(10.45)		61.39(61.67)		27.39(27.89)
5c	$C_5Cl_8F_2S_5$	(542.00)	11.26(11.08)		52.08(52.33)		29.32(29.58)
5d**	$C_5Cl_6F_4S_5$	(509.09)	11.94(11.80)		43.36(41.78)		28.60(31.49)
6b	$C_5Cl_{10}OS_5$	(590.91)	10.64(10.16)		59.37(60.00)		26.85(27.13)
9	$C_{14}Cl_{10}S_5$	(683.01)	25.07(24.62)		51.34(51.91)		22.16(23.47)*
17	$C_9H_7Cl_3S_4$	(349.77)			29.71(30.41)		36.60(36.67)
22b	$C_5Cl_{12}S_5$	(645.81)	9.71(9.30)		65.24(65.88)		24.69(24.82)
22c	$C_5Cl_{10}F_2S_5$	(612.90)	10.09(9.79)		57.28(57.84)		26.06(26.16)
24a	$C_3Cl_8S_5$	(479.98)	7.72(7.51)		59.31(59.09)		32.95(33.40)
24b	$C_5Cl_{12}S_5$	(654.81)	9.63(9.30)		64.83(65.88)		23.49(24.82)*
25	$C_{11}H_8Cl_7NO_2S_5$	(594.69)	22.47(22.22)	1.46(1.36)	41.60(41.73)	2.41(2.36)	26.80(26.96)
26	$C_9H_7Cl_5S_4$	(420.68)	25.95(25.70)	1.72(1.68)	42.19(42.14)		30.37(30.49)
28b	$C_5Cl_{12}S_6$	(677.88)	9.43(8.86)		63.50(62.76)		26.97(28.38)*
29a	$C_4Cl_{10}S_6$	(594.96)	8.24(8.08)		58.94(59.59)		31.93(32.34)
29b	$C_7Cl_{16}S_6$	(843.71)	10.83(9.97)		66.81(67.23)		22.10(22.80)
29c	$C_7Cl_{13}F_3S_6$	(794.35)	11.12(10.58)		57.63(58.02)		23.70(24.22)
30b	$C_7Cl_{16}S_7$	(875.78)	10.03(9.60)		64.09(64.77)		25.34(25.63)
31a	$C_4Cl_{10}S_9$	(691.15)	7.12(6.95)		50.95(51.29)		41.40(41.75)

* The sulfur determinations marked with an asterisk are too low by more than the accepted 1% deviation. However, the remaining elemental analytical and the spectral data, etc. fully support our structural assignments.

** Crude product.

TABLE 3. Bond lengths, angles and torsion angles (numerical value). Corresponding values for different branches are on the same line. Standard deviations in terms of the last digit are given in parentheses

Bond	5a		29a			31a
C=S	1.581(12)					
C-Cl				1.74(4)		1.763(6)
$C-S_1$	1.780(12)	1.789(10)	1.833(4)	1.826(3)	1.844(4)	1.820(2)
S_1-S_2	2.031(4)	2.023(5)	2.027(1)	2.022(1)	2.001(2)	2.046(1)
S_2-S_3						2.030(1)
S-C	1.815(12)	1.847(12)	1.826(4)	1.827(4)	1.850(4)	1.821(4)
C-Cl	1.772(12)	1.736(12)	1.762(4)	1.756(4)	1.748(5)	1.764(4)
	1.746(13)	1.782(12)	1.740(4)	1.751(4)	1.760(4)	1.753(4)
	1.793(12)	1.745(13)	1.760(4)	1.771(4)	1.766(4)	1.759(4)
Angle						
S=C-S	130.0(6)	116.2(7)				
Cl-C-S			116.5(2)	116.7(2)	113.6(2)	113.3(2)
S-C-S	113.6(6)		102.5(2)	101(7(2)	103.8(2)	105.4(2)
C-S-S	100.3(4)	109.0(4)	105.0(1)	106.1(1)	108.6(1)	103.7(1)
S-S-S						105.8(1)
S-S-C	100.9(4)	104.3(4)	102.6(1)	101.9(1)	108.7(1)	102.0(1)
S-C-Cl	113.1(6)	112.9(6)	110.9(2)	111.5(2)	113.1(2)	103.5(2)
	114.0(7)	110.6(6)	115.2(2)	114.4(2)	111.5(2)	112.9(2)
	102.1(6)	103.2(6)	103.4(2)	102.9(2)	103.2(2)	111.8(2)
Torsion angle						
$S=C-S_1-S_2$	11.4(8)	177.8(5)				
$Cl-C-S_1-S_2$			126.8(2)	128.0(2)	137.5(2)	53.3(1)
$C-S_1-S_2-X$	99.2(5)	97.4(5)	113.3(2)	112.9(2)	91.4(2)	95.4(1)
$S_1-S_2-S_3-C$						91.6(1)
S-S-C-Cl	61.0(7)	63.7(7)	66.3(2)	56.4(2)	26.6(2)	179.3(1)
	64.0(6)	59.1(6)	56.3(2)	67.4(2)	97.4(2)	60.6(2)
	177.4(4)	175.7(4)	176.7(2)	173.2(2)	145.9(2)	62.9(2)

EXPERIMENTAL

Technical grade trichloromethanesulfenyl chloride 4a was purified by vacuum distillation. Trichloromethylthiosulfenyl chloride 20a,[25] aqueous sodium trithiocarbonate (approx. 10 mol l^{-1}),[26a] and barium trithiocarbonate [8] were prepared by literature methods. Pentachloroethylthiosulfenyl chloride 20b was prepared by chlorination of acetyl pentachloroethyl disulfide.[26b] 1,1,2,2-Tetrachloro-2-fluoroethanesulfenyl chloride 4c and 1,1,2-trichloro-2,2-difluoroethanesulfenyl chloride 4d were a gift from A/S Cheminova, Lemvig, Denmark.

Infrared spectra were recorded on a Nicolet MX-S FT-IR spectrophotometer; ^{1}H NMR: Varian EM-360 60 MHz spectrometer, TMS as internal standard; ^{13}C NMR: Varian CFT-20 20 MHz spectrometer, the spectra were recorded overnight and chromium(III) tris(acetylacetonate)(50 mg per sample) was added except in cases (22 and 28) where it could be suspected to react.[27] Elemental analyses were carried out by Mikroanalytisk Laboratorium, Løvens Kemisk Fabrik, DK-2750 Ballerup, Denmark.

CAUTION: Attention is drawn to the irritant and toxic properties of many of the chemicals employed in this investigation, e.g. of thiophosgene, perhaloalkanesulfenyl chlorides 4 (4a is extremely toxic), carbon disulfide (extremely flammable and very toxic), chlorine, sulfuryl chloride, and sulfur dichloride.[28,29] The primary hazard is from inhalation of vapor. Avoid any contact with skin and eyes. Glassware contaminated with the sulfenyl chlorides 4 should be rinsed with a mixture of aqueous ammonia and alcohol.

Bis(perhaloethyl)pentathiodipercarbonates 5

Method B: A mixture of the sulfenyl chloride 4 (typically 0.001-0.01 mol) and barium trithiocarbonate (10% excess) in acetonitrile (approximately 50 ml/mol) is stirred at ambient temperature for 18 h. The solvent is evaporated in vacuo and the residue extracted with water and methylene chloride. The organic layer is dried over $CaCl_2$ and charcoal and the solvent evaporated in vacuo. If the crude product does not solidify spontaneously crystallization may be induced by addition of acetone and cooling to -25 °C.

Reaction of 7 with Na_2CS_3

Aqueous sodium trithiocarbonate (5.3 mmol) was added with stirring to a solution of dichloro-(pentachlorophenylthio)methanesulfenyl chloride 7 [30] (1.53 g, 3.5 mmol) in 10 ml of methylene chloride. After 30 min a pink precipitate was filtered off. The CH_2Cl_2 phase was washed three times with 30 ml of water, dried over $CaCl_2$ and evaporated to give 0.58 g of mainly pentachlorophenyl chlorodithioformate 8 [30] (46%, based on 7).

Dissolution of the precipitate in hot chloroform led to decolorization. Recrystallization of part of the pink material (7%) gave 0.014 g of orange crystals of 9. At 130 °C a decolorization occurs and the resulting substance melts at 149-160 °C.

Reaction of pentachlorobenzenesulfenyl chloride 10 with Na_2CS_3

A solution of 10 [31] (12.3 g, 39 mmol) in 150 ml of methylene chloride was added rapidly to a stirred solution of aqueous sodium trithiocarbonate (19 mmol) at 0-5 °C and the mixture was stirred for 3 h. A precipitate was filtered off and dried to give 8.60 g (76%) of bis(pentachlorophenyl) trisulfide 11, mp. 193-196 °C. From the methylene chloride solution was obtained 1.84 g (16%) of 11. Recrystallization from tetrachloromethane gave yellowish crystals, mp. 195-197 °C. (lit.[9] mp. 192.5-194.5 °C). The IR (KBr) and the mass spectra of 11 are practically identical with those of bis(pentachlorophenyl) disulfide [32] (lit.[9] mp. 237 °C) except for a weak molecular peak of 11 at m/e 590.

Reaction of p-toluenesulfenyl chloride with Na_2CS_3

A benzene solution of p-toluenesulfenyl chloride [33] (43 mmol) and aqueous sodium trithiocarbonate (22 mmol) was mixed rapidly at 0-5 °C and stirred for 30 min. Then the benzene layer was dried over $CaCl_2$ and evaporated in vacuo to give an orange oil (6.51 g); IR (film): $\nu_{C=S}$ 1055 (vs) cm^{-1}. A part of the crude product (5.69 g) was subjected to column chromatography on silica gel with a 9:1 mixture of petroleum ether and methylene chloride as eluent. Fraction I: Pale yellow crystals of bis(p-tolyl) trisulfide 12 (3.73 g, overall yield 71%), mp. 60-75 °C. One recrystallization from benzene gave colorless plates, mp. 79-81 °C (lit.[34a] 81-82 °C); ^{1}H NMR ($CDCl_3$): (AB approximation) δ_A 7.36, δ_B 7.04 (5H,J_{AB} 8Hz), 2.27 (s,2H). Fraction II: Dark yellow substance (0.39 g); shows two spots (12 and a yellow component) on TLC; IR (KBr): $\nu_{C=S}$ 1060 cm^{-1}; the ^{1}H NMR spectrum is practically identical with the spectrum of 12.

Fractions III: Pure bis(p-tolyl) trithiocarbonate (0.14 g, overall yield 2.6%); yellow needles, mp. 113-116 °C (lit.[35] mp. 114-116 °C); m/e 290($M^{+\cdot}$), 167($ArSCS^+$), 123(ArS^+); IR (KBr): $\nu_{C=S}$ 1090 cm^{-1}.

Attempted synthesis of 15

The reaction eq.(9), was carried out according to Himel and Edmonds.[1d] Scale 21 mmol. A quantitative yield (4.45 g) of bis(p-tolyl)disulfide 16 was obtained, colorless needles, mp. 40-47 °C. One recrystallization from ethanol gave mp. 45-46 °C (lit.[10b] 47-48 °C), IR [18] and ^{1}H NMR [3b] data are in agreement with the literature.

S-Phenylmethyl SS-trichloromethyl tetrathiopercarbonate 17

Phenylmethanethiol (24.8 g, 0.20 mol) was added dropwise during 30 min with stirring at 15 °C to potassium hydroxide (11.2 g, 0.20 mol) in 150 ml of ethanol. After stirring for 30 min carbon disulfide (15.2 g, 0.20 mol) was added with stirring at 15 °C during 30 min and the mixture was subsequently stirred at 25 °C for 3 h. The solution thus prepared was added during 1 h at 0-5 °C to a stirred solution of trichloromethanesulfenyl chloride (37.2 g, 0.20 mol) in methylene chloride.

The solvent was evaporated in vacuo and the residue dissolved in methylene chloride/water. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give 61 g (81%) of crude 17. Recrystallization from acetone gave 41.2 g (59%) of 17. ^1H NMR ($CDCl_3$): δ 7.18 (s,5H) and 4.43 (s,2H).

1,2,3,5,6-Pentathiepane (lenthionine) 19

The unknown 18 was the desired product from the reaction eq.(11) and the yield of the actual product 19 was not optimized. A good yield was obtained as follows: Sodium tetrathiopercarbonate[37] (0.10 mol) in 40 ml of ethanol was treated with ether (350 ml all together) in order to precipitate the salt in crystalline form.[37] No crystallization occurred and so the mixture was used as such. Methylene iodide (27.3 g, 0.10 mol) in 100 ml of ethanol was added with stirring and when all of the precipitate had dissolved 750 ml of water was added. The ether layer was separated and washed three times with water, dried over $CaCl_2$ and evaporated in vacuo to give 13.7 g of an odorous yellow oil.

Column chromatography (silica gel/petroleum ether) of 4.10 g of the product yielded 2.13 g of CH_2I_2 and 1.52 g of lenthionine (overall yield 53% based on the total amount of CH_2I_2) mp. 52-54 °C.

Lenthionine (0.94 g, overall yield 25%) precipitated at -25 °C from 5.3 g of the crude product dissolved in 15 ml of acetone. One recrystallization from methylene chloride yielded 0.62 g, mp. 58-61 °C (lit.[12a] 60-61 °C). IR,[12a] ^1H NMR,[12b] and mass spectral data [12a] are in agreement with the literature. ^{13}C NMR ($CDCl_3$): δ 52.1.

Rearrangement of the sulfenyl chlorides 22

In acetonitrile: A suspension of 22a (1.03 g) in 20 ml of acetonitrile was stirred at room temperature for 7 days. The mixture was cooled to -25 °C and the precipitate filtered off and dried to give 0.58 g of almost pure dichloro(trichloromethyldithio)(trichloromethyltrithio)methane 24a, mp. 45-49 °C.

In chloroform: To a solution of 22b (0.37 g, pure judging from the ^{13}C NMR spectrum recorded overnight) in 2 ml of $CDCl_3$ a few crystals of $HgCl_2$ were dissolved at room temperature. After three days the solvent was evaporated in vacuo and the residue crystallized from acetone yielding 0.20 g of dichloro(pentachloroethyldithio)(pentachloroethyltrithio)methane 24b, mp. 83-86 °C.

Reaction of 22a with Δ^4-tetrahydrophthalimide[38]

The sulfenyl chloride 23a (4.80 g, 10 mmol) and a few mg of tetrabutylammonium tetrafluoroborate in 20 ml of methylene chloride were added with stirring during 30 min to a solution of Δ^4-tetrahydrophthalimide (1.51 g, 10 mmol) and sodium hydroxide (0.4 g) in 20 ml of water at 0-5 °C. The mixture was stirred for 30 min, the organic layer separated, washed three times with water, dried over $CaCl_2$, and evaporated in vacuo. Recrystallization of the residue from ether gave 3.0 g (5 mmol) of N-[chlorobis(trichloromethyldithio)methylthio]-4-cyclohexene-1,2-dicarboximide 25, mp. 110-115 °C. Two more recrystallizations gave an analytically pure sample.

Chlorination of 17

Excess sulfuryl chloride (1 ml) was added to a solution of the tetrathiopercarbonate 17 (0.37 g, 1.1 mmol) in 10 ml of methylene chloride at room temperature. As soon as the yellow color of 17 had disappeared the mixture was evaporated to give 0.44 g (98%) of slowly crystallizing 27, mp. 43-45 °C. Two recrystallizations from petroleum ether gave analytically pure chloro(phenylmethylthio)(trichloromethyldithio)methanesulfenyl chloride 27.

A freshly prepared $CDCl_3$ solution of 27 is almost colorless. Besides the two singlets in the ^1H NMR spectrum listed in Table 1 a weak singlet at 4.33 ppm is seen. After a few minutes the solution becomes yellow. After three hours the ratio I_2:I_1 of the integrals of the signals δ_2 4.33 and δ_1 4.13 is approximately 3:1. After one day a third singlet δ_3 4.50 appears and after several days δ_3 becomes dominant.

S-Sulfenylation of thiocarbonyl compounds

Tris(disulfides), example: A suspension of the pentathiodipercarbonate 5b (1.64 g, 2.9 mmol) and the sulfenyl chloride 4b (0.77 g, 2.9 mmol) in 10 ml of acetonitrile was stirred and heated to reflux for 17 h. The mixture was then cooled to room temperature and crude 29b was filtered off and dried (1.96 g, 81%). One recrystallization from methylene chloride gave 1.35 g (56%) of chlorotri(pentachloroethyldithio)methane 29b, mp. 142-146 °C.

Alternatively the reaction may be carried out at room temperature by stirring the reactants in acetonitrile for about 7 days.

Tris(trisulfide) 31a: Trichloromethylthiosulfenyl chloride 20a (1.15 g, 5.3 mmol) and barium trithiocarbonate (0.65 g, 2.6 mmol) in 20 ml of acetonitrile was stirred at room temperature overnight. Methylene chloride (75 ml) and water (100 ml) was added, the organic layer was separated and washed with water, dried over $CaCl_2$, and evaporated in vacuo. Recrystallization from ether/CH_2Cl_2 (2:1) gave 0.157 g of chlorotris(trichloromethyltrithio)methane 31a as colorless needles. Based on the relatively high intensity of the ^{13}C NMR ($CDCl_3$) signal at δ 99.7 (Table 1) it is assigned the CCl_3 group of 31a. Signals each of approx. one fourth of the intensity of $\delta(CCl_3)$ appear at δ 99.4 and 98.9. The latter is tentatively asigned the central carbon of 31a and the former might be due to a decomposition product, e.g. 21a.

Either of two modifications I and II of 31a may be isolated by recrystallization and distinguished by their thermal behaviour.

Modification I: A transition in the solid state from relatively long to much smaller needles at 79-81 °C is visible in a melting point apparatus with a microscope (starting temperature 40 °C, heating rate 3 °C min^{-1}). The resulting crystals melt at 129-140 °C. Starting at 110 °C the needles (I) immediately melt and subsequently crystallize, mp. 125-135 °C.

Modification II: The needles become opaque at 125 °C and melt at 130-140 °C.

X-Ray work

Preliminary cell dimensions and symmetry were determined from precession- and Weissenberg photographs. Cell dimensions were determined from the setting angles of 24 (5a), 29 (23a), and 18 (31a) reflexions, respectively. The data were collected on an automatic Picker FACSI diffractometer with Zr-filtered MoKα radiation. Step scans were collected and integrated according to the minimum δ(I)/I criterion,[39] the data were corrected for Lorentz- and polarization effects but not for absorption. Averaging produced 2237, 3445, and 2782 reflexions out of 7093, 3815, and 8037 measured; of these 1266, 2640, and 971 had I > 3 δ(I) and were used in the refinements. The atomic positions were found by means of MULTAN [40] and refined by full matrix least squares [41] together with anisotropic thermal parameters. The crystals of 5a were twinned such that hkl of one twin coincided with -h-2ℓ,k,ℓ of the other twin. This was included in the refinement and the relative amount of the twins was included as a parameter, converging at 1:0.224. The poor crystal quality limits the accuracy of this structure. The final R-values are 0.075, 0.035 and 0.025, respectively. Final coordinates and equivalent isotropic thermal parameters are given in Table 4. Lists of observed and calculated structure factors are deposited with the British Library Lending Division.

TABLE 4. Coordinates ($*10^5$) and equivalent isotropic temperature factor ($*10^4$)

Bis(trichloromethyl) pentathiodipercarbonate 5a

	x	y	z	u_{iso}
S	74586(16)	15294(29)	84(63)	615(20)
S1	82762(14)	21379(24)	48558(51)	503(18)
S2	83778(14)	36946(25)	29406(57)	524(19)
S3	76749(15)	-3881(27)	35944(65)	627(21)
S4	81431(15)	-5940(28)	69971(58)	591(21)
Cl1	91329(15)	19460(31)	8873(62)	689(22)
Cl2	96970(16)	33591(35)	50397(66)	795(24)
Cl3	92000(19)	47008(36)	6534(76)	930(29)
Cl4	92776(15)	-5539(32)	54576(64)	729(24)
Cl5	86579(18)	-29359(29)	53911(69)	800(25)
Cl6	92016(20)	-17103(37)	98012(59)	901(28)
C	78087(48)	11752(94)	26164(198)	458(67)
C1	91108(53)	33784(111)	24639(219)	577(78)
C2	88354(54)	-14392(101)	68507(208)	548(73)

Chlorotris(trichloromethyldithio)methane 29a

	x	y	z	u_{iso}
S1	34720(5)	12628(17)	66166(5)	419(5)
S2	42964(5)	27179(20)	73895(6)	481(6)
S3	27096(5)	11587(16)	49817(5)	388(5)
S4	18198(5)	24565(19)	52106(6)	462(6)
S5	42282(5)	14382(19)	53813(6)	460(6)
S6	44120(6)	31537(21)	44482(6)	528(6)
Cl1	34750(8)	24032(23)	86324(7)	733(8)
Cl2	32267(8)	61640(24)	76023(7)	767(9)
Cl3	45710(7)	56648(30)	87068(9)	939(10)
Cl4	13128(6)	20985(20)	34484(6)	578(6)
Cl5	19214(7)	62456(20)	40851(8)	736(8)
Cl6	6056(7)	47869(30)	44106(8)	855(9)
Cl7	38296(7)	-11259(20)	36356(7)	673(8)
Cl8	31362(6)	30186(26)	30955(7)	722(8)
Cl9	45227(6)	21921(24)	28639(7)	683(8)
Cl	34126(6)	55321(16)	56338(6)	475(6)
C	34395(18)	26135(59)	56484(20)	351(19)
C1	38680(20)	42570(70)	80648(21)	456(23)
C2	14377(21)	39186(72)	42747(23)	471(22)
C3	39524(21)	17436(73)	35114(23)	477(23)

Chlorotris(trichloromethyltrithio)methane 31a

	x	y	z	u_{iso}
S1	4215(6)	-6059(6)	6256(14)	422(5)
S2	15509(6)	-1393(6)	-1596(17)	512(5)
S2	13741(6)	-8906(6)	-15406(15)	473(5)
Cl	0(0)	0(0)	-15400(0)	681(4)
Cl1	14637(9)	-23123(8)	-20884(18)	729(7)
Cl2	26102(7)	-12111(10)	-3728(19)	807(9)
Cl3	9006(7)	-22193(7)	2121(16)	585(6)
C	0(0)	0(0)	-15(49)	437(19)
C1	15985(21)	-16507(23)	-9079(34)	456(19)

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