Polyhalogenated BEDT-TTF through chlorination (SO_2Cl_2, Cl_2) and fluorination (®Selectfluor, XeF_2) of 5,6-dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one

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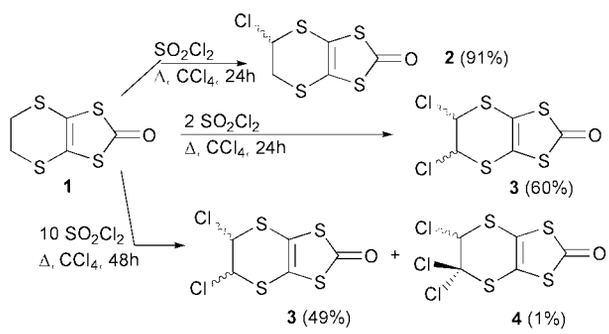
The electrophilic halogenation of the ethylenic bridge in the 5,6-dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one (**1**) with SO_2Cl_2, ®Selectfluor [1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)] or XeF_2 affords the corresponding monochloro, 1,2-dichloro and monofluoro derivatives **2**, **3** and **6**, respectively. Reaction with Cl_2 gives rise to a pentachloro derivative (**5**) with *syn*-Cl_2 addition across the unsaturated double bond of **1** characterised by single crystal X-ray diffraction. Homocoupling of **2**, **3** or **6** in $P(OMe)_3$ affords the corresponding dichloro, tetrachloro and difluoro BEDT-TTFs **8**, **9** and **10**, respectively, whose electrochemical characteristics show the electron-withdrawing nature of the halogen substituents present on the ethylenic bridge. Electrocrystallisation of **9** in the presence of $(n\text{-}Bu_4N)_2(Mo_6Cl_{14})$ affords a mixed-valence salt formulated as $[\mathbf{9}]_3[Mo_6Cl_{14}]$, whose X-ray crystal structure has been determined and analysed.

Introduction

In a previous communication,[1] we have described our first results concerning the halogenation of 5,6-dihydro[1,3]dithiolo-[4,5-*b*][1,4]dithiin-2-one (**1**). This heterocycle is the starting material for the preparation of (i) the well known bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) through $P(OR)_3$ coupling, (ii) the $dddt^{2-}$ dithiolene complexes. Its halogenated derivatives offer therefore numerous opportunities for the preparation of novel conducting materials based on halogenated tetrathiafulvalenes and dithiolene complexes. We were indeed attracted by the possibilities offered by halogen ··· halogen interactions[2,3] in the solid state to control the solid state organisation of molecular conductors. They are characterised by Hal ··· Hal distances significantly shorter than the sum of the van der Waals radii of the contacting atoms and are mainly observed with the most polarisable halogens (I > Br > Cl). One can take advantage of these interactions in conducting cation radical salts of bromo and iodo tetrathiafulvalenes where such short Hal ··· Hal contacts contribute to, not only the structural organisation, but also the electronic delocalisation.[4,5] Fluorine atoms, because they are very poorly polarisable, do not afford such F ··· F interactions[6] but can lead to layered structures with a segregation of the fluorinated and non-fluorinated moieties, as observed in soft matter chemistry of amphiphilic molecules or in fluorinated bis(propylenedithio)-tetrathiafulvalenes.[7,8] In this article we describe the chlorination of **1** to afford polychlorinated derivatives, fluorination of **1** to the monofluoro derivative and the coupling of the products to the corresponding dichloro-, tetrachloro- and difluoro-BEDT-TTF donor molecules.

Results and discussion

As already described in a previous communication,[1] the chlorination of 5,6-dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one (**1**) with one or two equiv. SO_2Cl_2 afforded the corresponding mono- and dichloro derivatives **2** and **3**, respectively (Scheme 1). In an attempt to pursue further this halogenation toward the tri- and tetrachloro derivatives, the same reaction was performed under more stringent conditions with 10 equiv. SO_2Cl_2 during 48 h. The dichloro compound **3** was obtained together with only a very small amount of the trichloro compound **4**. The latter crystallises from CCl_4, and its identity was confirmed by the usual methods and its geometry determined from an X-ray crystal structure (Fig. 1). The molecule with one stereogenic center at the C4 atom with only one chlorine atom is located in a general position in the centrosymmetric unit cell (space group *C*2/*c*). It therefore crystallises as the racemic mixture of both (*R*) and (*S*)-enantiomers. Furthermore, the carbon atoms (C3 and C4) of the ethylene bridge are disordered on two positions as observed in **3** in a 80 : 20 ratio. It clearly appears



Scheme 1

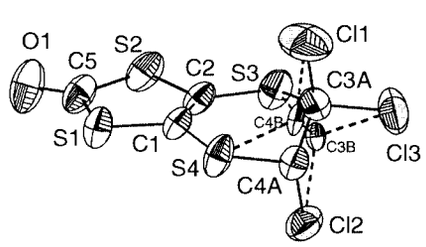
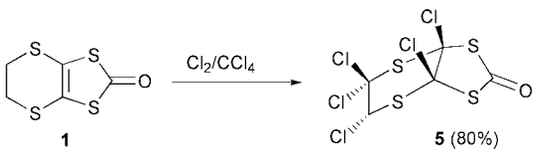


Fig. 1 ORTEP view of **4** (thermal ellipsoids are represented at 50% probability level).

that once a chlorine atom is in the α-position, the neighbouring thioether function is strongly deactivated to reaction with a second Cl^+ equivalent to afford the *gem*-dichloro derivative.

The perchlorination of **1** was further attempted with gaseous Cl_2. One single compound was isolated in 80% yield and proved to be the pentachloro addition compound **5** (Scheme 2). Not



Scheme 2

only has the ethylene bridge been trichlorinated but we also observe addition of Cl_2 across the double bond. The stereochemistry of the compound, which has been obtained in a crystalline form by evaporation, was deduced from a X-ray crystal structure determination (Fig. 2). Since the molecule crystallises

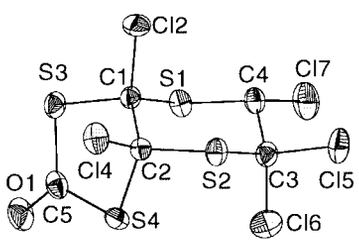
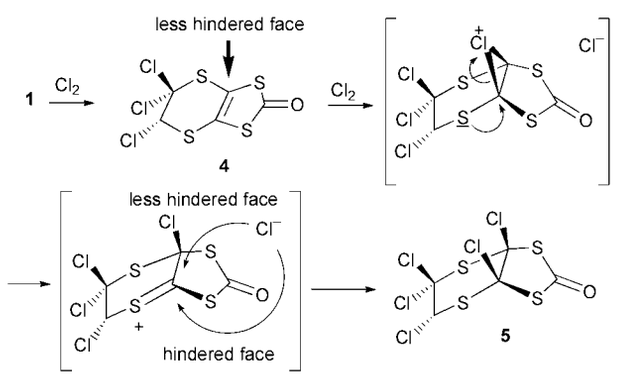


Fig. 2 ORTEP view of the (3a*R*,7a*S*,6*R*)-enantiomer of **5** (thermal ellipsoids are represented at 50% probability level).

in a centrosymmetric space group, this compound has been obtained as a racemic mixture of the two enantiomers, also characterised by a *syn*-addition of Cl_2 on the unsaturated double bond. As shown in Scheme 3, if the chlorination of the



Scheme 3

ethylene bridge is performed first, as one would expect from the products obtained with milder chlorinating reagents than Cl_2 (see above), the addition of chlorine on the double bond most probably occurs on the less hindered side of **4** to afford a cyclic chloronium. The usual *trans* addition of the Cl^- anion is not observed here but a *syn* addition occurs instead. There might be two good reasons for this behaviour: (i) formation of the chloronium on this bridged bicycle leads to a severe folding and the *trans*-addition becomes strongly hindered, (ii) the chloronium cation is not symmetrical and might afford a open carbocation stabilised by delocalisation on the neighbouring thioether group. Such *syn* additions have been already observed on phenyl substituted alkenes for example.[9]

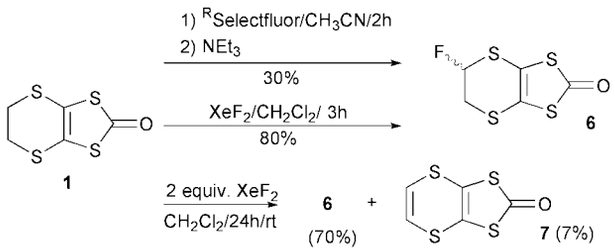
The fluorination of **1** was also investigated. Different sources of electrophilic fluorine are available and among them ®Selectfluor [1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo-

Table 1 Cyclic voltammetry data

Donor	$E_1^{1/2}/V$ (ΔE_1)	$E_2^{1/2}$ (ΔE_2)
BEDT-TTF[a]	0.49	0.74
8	0.58 (67 mV)	0.82 (64 mV)
9	0.66 (67 mV)	0.88 (63 mV)
10	0.58 (66 mV)	0.82 (60 mV)

[a] See Ref. 15

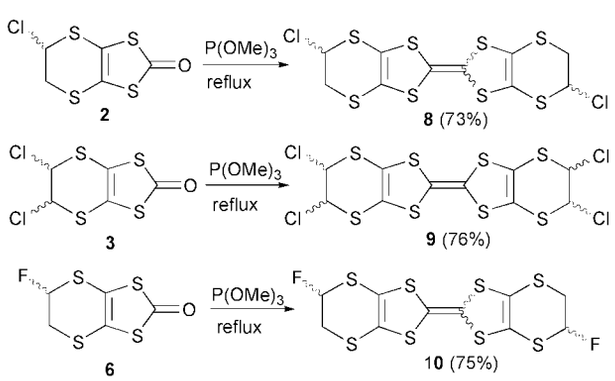
[2.2.2]octane bis(tetrafluoroborate)] has proved a convenient and stable compound.[10] Reaction of **1** (Scheme 4) with one



Scheme 4

equiv. of ®Selectfluor, followed by addition of NEt_3, afforded the desired monofluoro compound **6** in 30% yield. Reaction with two equiv. did not improve the reaction while the added NEt_3 reacted with the dithiocarbonate function, as evidenced by the red coloration characteristic of the formed dithiolene salts. XeF_2 offers an alternative to the ®Selectfluor–NEt_3 system since the fluoride anion liberated after F^+ addition on the thioether plays the role of the base. Reaction of XeF_2 with **1** afforded **6** in a much better yield (80%). Prolonged reaction with two equiv. XeF_2 (Scheme 4) in order to obtain the corresponding difluoro derivative only led to partial degradation of **6** which eliminates HF to form the vinylene derivative **7** in 7% yield after 24 h stirring, together with 70% of **6**. Note that the vinylic compound **7** was also obtained from **2** upon KF–10-crown-6 treatment.[1]

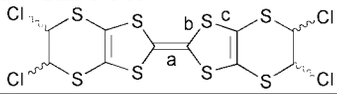
The three monochloro, dichloro- and monofluoro derivatives **2**, **3** and **6** can be converted into the corresponding tetrathiafulvalenes in boiling $P(OMe)_3$, affording the dichloro-, tetrachloro and difluoro BEDT-TTF **8**, **9** and **10**, as a mixture of isomers in good yields (Scheme 5). Cyclic voltammetry experiments show



Scheme 5

that the three donor molecules oxidise reversibly to the mono- and dication (Table 1). An anodic shift due to the electron-withdrawing nature of the halogen atoms is clearly observable, and increases with the number of halogen atoms present. This shift is however very limited and does not hinder the possibility to grow cation radical salts with these novel donor molecules. Preliminary electrocrystallisation experiments were performed with the tetrachloro derivative **9** and various anions such as

Table 2 Averaged important bond distances in the crystallographically independent $\mathbf{9}_A$ and $\mathbf{9}_B$ molecules in $[\mathbf{9}]_3[Mo_6Cl_{14}]$ and in the neutral and oxidised BEDT-TTF



	C=C bond (a)/Å	C–S bond (b)/Å	C–S bond (c)/Å
BEDT-TTF^0	1.343(4)	1.756(3)	1.760(3)
$\mathbf{9}_A$	1.357(15)	1.747(11)	1.748(11)
$\mathbf{9}_B$	1.381(11)	1.717(8)	1.736(14)
BEDT-TTF$^{+\bullet}$	1.386(6)	1.719(10)	1.734(10)

PF_6^-, ReO_4^-, I_3^- and $Mo_6Cl_{14}^{2-}$. With the latter, a 3 : 1 phase formulated as $[\mathbf{9}]_3[Mo_6Cl_{14}]$ was obtained as plate-shaped crystals and its X-ray crystal structure was determined. The dianionic molybdenum clusters are located on the inversion centre at the cell corners while three donor molecules are associated to form dicationic trimers at the centre of the unit cell (Fig. 3).

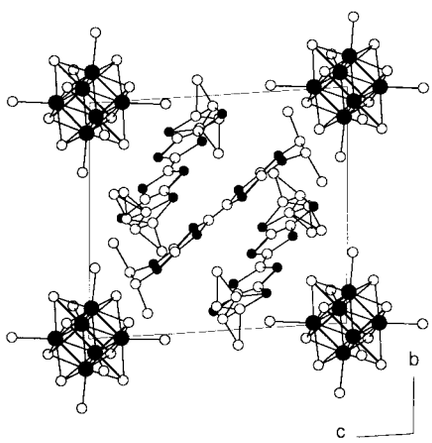


Fig. 3 A projection view along the a axis of the unit cell of $[\mathbf{9}]_3[Mo_6Cl_{14}]$.

Molecule $\mathbf{9}_A$, located on the inversion centre, exhibits no disorder of the dichloroethylene bridge while molecule $\mathbf{9}_B$, in general position, exhibits a disordered bridge (Fig. 4). Of

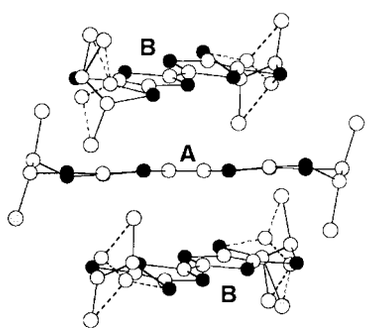


Fig. 4 A view of the trimeric entities with the disordered ethylenic bridges in $\mathbf{9}_B$.

particular note is the very unusual criss-cross overlap within the trimers, attributable to the steric hindrance of the chlorine atoms. Comparison of the bond distances within the TTF core between molecules $\mathbf{9}_A$ and $\mathbf{9}_B$ and with reference compounds such as neutral BEDT-TTF[11] or oxidised[12] BEDT-TTF$^{+\bullet}$ (Table 2) shows that most of the dicationic charge is concentrated on the two outer $\mathbf{9}_B$ molecules while molecule $\mathbf{9}_A$ is almost neutral. Note that this electronic repartition is quite unusual in such TTF triads where most often a TTF$^{+0.5}$-TTF^{+1}-TTF$^{+0.5}$ structure is found.[13,14] It expresses here the weak interaction between the three molecules due to the criss-cross organisation, and hence a charge localisation (in the B molecules) rather than a delocalisation over the whole triad.

Electrocrystallization experiments with the three donors are now under investigation as well as the syntheses of unsymmetrically substituted BEDT-TTF incorporating the halogen atoms on only one side of the molecule in order to favour intermolecular overlap for an extended electronic delocalisation.

Experimental

General considerations

Unless otherwise indicated, all reactions were carried out under nitrogen. Solvents (dichloromethane, acetonitrile) were dried and freshly distilled over P_2O_5. Note that DAST and related dialkylaminosulfur trifluorides should not be heated since they are said to undergo catastrophic decomposition (explosion or detonation) with gas evolution upon heating above 90 °C.[16] ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at 200 (^{1}H, ^{19}F) and 50 MHz (^{13}C). The chemical shifts are given in δ ppm, downfield from internal Me_4Si for ^{1}H and ^{13}C NMR, upfield from external $CFCl_3$ for ^{19}F NMR. Mass spectra were taken in the EI mode with an ionization energy of 70 eV and a current intensity of 300 μA. Cyclic voltammetry measurements were taken with a Pt disk ($\varnothing$ = 1 mm) as working electrode and a Pt wire as counter electrode and a SCE as reference electrode. Elemental analyses were performed either at the Service Central d'Analyse (CNRS), Vernaison, France or the Institut de Chimie des Substances Naturelles (CNRS), Gif/Yvette, France.

5,5,6-Trichloro-5,6-dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one 4

To a solution of the dithiocarbonate **1** (2 g, 9.6 mmol) in CCl_4 (50 mL) at reflux was added dropwise a solution of SO_2Cl_2 (10 equiv., 7.7 mL, 96 mmol) in CCl_4 (50 mL). After refluxing for 48 h, the solution was cooled and concentrated under reduced pressure. SiO_2 chromatography (eluent: cyclohexane–CH_2Cl_2 2 : 1) and recrystallisation from CCl_4 afforded **3** (1.3 g, 49%) as cream platelets and **4** (0.03 g, 1%). **4**: mp 72 °C (CCl_4); R_f 0.6 (CH_2Cl_2–cyclohexane 2 : 1); δ_H (200 MHz; $CDCl_3$) 5.83 (s, 1H, C*H*Cl); δ_C (50 MHz; $CDCl_3$) 68.6 (*C*HCl), 88.1 (*C*Cl_2), 110.5 (*C*=C), 112.1 (C=*C*), 186.8 (C=O); *m*/*z* (EI) 313 (23%), 312 (5), 311 (50 M^+), 152 (67), 88 (85), 76 (100).

3a,5,5,6,7a-Pentachloro-tetrahydro[1,3]dithiolo[4,5-*b*]dithiin-2-one 5 (as racemic mixture of the (3a*R*,7a*S*,6*R*) isomer and its enantiomer)

Gaseous Cl_2 was passed through a solution of the dithiocarbonate **1** (1 g, 4.8 mmol) in CCl_4 (100 mL) at room temperature during 24 h. Concentration and recrystallisation from CCl_4 afforded **5** (1.5 g, 80%) as white unstable crystals. Satisfactory elemental analysis could therefore not be obtained. Mp 96 °C; δ_H (200 MHz, $CDCl_3$) 5.77 (s, 1H, C*H*C); δ_C (50 MHz, $CDCl_3$) 68.2 (CHCl), 187.2 (*C*=O); *m*/*z* (EI) 384 (3%), 382 (3, M^+), 253 (64), 152 (45), 88 (100), 76 (96).

Bis(chloroethylenedithio)tetrathiafulvalene 8

A solution of **2** (240 mg, 1 mmol) in freshly distilled $P(OMe)_3$ (7.5 mL, 60 equiv.) was warmed to reflux for 3 h. After cooling, toluene was added and the solution evaporated under reduced pressure to eliminate the phosphite. SiO_2 chromatography (eluent: toluene) afforded **8** (165 mg, 73%), recrystallised from toluene (Found: C, 26.95; H, 1.25; S, 55.90. $C_{10}H_6Cl_2S_8$ requires C, 26.48; H, 1.33; S, 56.55%); mp 146–148 °C (dec.); δ_H

(400 MHz, $CDCl_3$) 3.31 and 3.34 (dd, 2H, CH_aH$_b$, $^2J_{HaHb}$ = 12.5 Hz, $^3J_{HaHc}$ = 7 Hz), 3.49 and 3.52 (dd, 2H, CH$_a$$H_b$, $^2J_{HaHb}$ = 12.5 Hz, $^3J_{HbHc}$ = 3 Hz), 5.72 (dd, 2H, C*H*Cl, $^3J_{HcHb}$ = 3 Hz, $^3J_{HcHa}$ = 7 Hz); *m*/*z* (EI) 453.55 (M^+, $C_{10}H_8Cl_2S_8$ requires 453.59), 416 (31%), 390 (36), 354 (37), 88 (100).

Bis(1,2-dichloroethylenedithio)tetrathiafulvalene 9

A solution of **3** (277 mg, 1 mmol) in freshly distilled $P(OMe)_3$ (7.5 mL, 60 equiv.) was warmed to reflux for 3 h. After cooling, toluene was added and the solution evaporated under reduced pressure to eliminate the phosphite. SiO_2 chromatography (eluent: toluene) afforded **9** (200 mg, 76%) recrystallised from toluene (Found: C, 24.28; H, 0.91; Cl, 25.37. $C_{10}H_4Cl_4S_8$ requires C, 22.99; H, 0.77; Cl, 27.14%, the higher C and H content, the lower Cl content indicate partial decomposition and HCl loss); mp >250 °C (dec); δ_H (400 MHz, $CDCl_3$) 5.47 (s, 2H, C*H*Cl); *m*/*z* (EI) 522.67 (M^+, $C_{10}H_4Cl_4S_8$ requires 522.48), 426 (47%), 354 (50), 88 (100).

5-Fluoro-5,6-dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one 6

Fluorination with ®Selectfluor. To a solution of **1** (0.5 g, 2.4 mmol) in dry CH_3CN (50 mL) is added ®Selectfluor (0.852 g, 2.4 mmol) and the solution stirred for 2 h at 30 °C. After addition of NEt_3 (0.334 mL, 2.4 mmol), the solution turned red, it was washed with H_2O, extracted with CH_2Cl_2 and dried with $MgSO_4$. Chromatography on SiO_2 (eluent: cyclohexane–CH_2Cl_2: 2 : 1) and recrystallization from CH_3CN afforded **6** (160 mg, 30%) as white crystals.

Fluorination with XeF_2. To a solution of **1** (0.5 g, 2.4 mmol) in dry CH_2Cl_2 (50 mL) was added XeF_2 (1 g, 5.9 mmol) and the solution was stirred at rt for 3 h. After a filtration on a SiO_2 column (eluent: CH_2Cl_2), the residue (600 mg) was chromatographed on SiO_2 (eluent: cyclohexane–CH_2Cl_2: 2 : 1) and recrystallised from CH_3CN to afford **6** (525 mg, 80%) as white crystals, mp 100 °C (Found: C, 26.40; H, 1.28; $C_5H_3FOS_4$ requires C, 26.53; H, 1.34%); ν_{max}(KBr)/cm^{-1} 1660 (C=C), 1613 (C=O), 1032 (CF); δ_H (200 MHz, $CDCl_3$) 3.30 (dt, 1H, CH_bH$_c$, $^3J_{HbF}$ = 14.0 Hz, $^2J_{HbHc}$ = 14 Hz, $^3J_{HbHa}$ = 2.3 Hz), 3.42 (m, 1H, CH$_b$$H_c$), 6.47 (ddd, 1H, C$H_a$F, $^2J_{HaF}$ = 52 Hz, $^3J_{HaHc}$ = 4.6 Hz, $^3J_{HaHb}$ = 2.3 Hz); δ_C (50 MHz, $CDCl_3$) 35.3 (d, S*C*H$_b$H$_c$, $^2J_{CF}$ = 23.6 Hz), 92.0 (d, S*C*FH$_a$, $^1J_{CF}$ = 225 Hz), 113.9 (s, *C*=*C*), 188.1 (s, *C*=O); δ_F (50 MHz, $CDCl_3$) −140.2 (s); *m*/*z* (EI) 226 (55%, M+), 198 (41), 88 (50), 76 (100).

Bis(fluoroethylenedithio)tetrathiafulvalene 10

A solution of **6** (120 mg, 0.5 mmol) in freshly distilled $P(OMe)_3$ (4 mL, 60 equiv.) was warmed to reflux for 3 h. After cooling, toluene was added and the solution evaporated under reduced pressure to eliminate the phosphite. SiO_2 chromatography (eluent: toluene) afforded **10** (75 mg, 75%) (Found: C, 29.48; H, 1.43; S, 59.85. $C_{10}H_6F_2S_8$ requires C, 28.55; H, 1.44; S, 60.98%); mp 210–212 °C (dec); δ_H (400 MHz, $CDCl_3$) 3.02 and 3.08 (ddd, 1H, CH_bH$_c$, $^3J_{HbF}$ = 14.0 Hz, $^2J_{HbHc}$ = 14 Hz, $^3J_{HbHa}$ = 2.3 Hz), 3.36 (m, CH$_b$$H_c$), 6.40 (ddd, 1H, C$H_a$F, $^2J_{HaF}$ = 50.6 Hz, $^3J_{HaHc}$ = 4.8 Hz, $^3J_{HaHb}$ = 2.3 Hz); δ_F (400 MHz, $CDCl_3$) −139.08 and −140.20; *m*/*z* (EI) 420.71 (M^+, $C_{10}H_8F_2S_8$ requires 420.68), 374 (86%), 254 (33), 210 (46), 88 (100).

Table 3 Crystallographic data

	4	**5**	[**9**]$_3$[Mo_6Cl_{14}]
Formula	$C_5HCl_3OS_4$	$C_5HCl_5OS_4$	$C_{15}H_6Cl_{13}Mo_3S_{12}$
M/g cm^{-3}	311.65	382.55	1317.57
Crystal system	Monoclinic	Monoclinic	Triclinic
a/Å	17.406(4)	6.5432(13)	10.217(2)
b/Å	6.3523(13)	16.283(3)	13.028(3)
c/Å	19.536(4)	11.420(2)	14.255(3)
α/°	90	90	93.10(3)
β/°	96.24(3)	94.81(3)	97.24(3)
γ/°	90	90	95.29(3)
U/Å^3	2147.2(8)	1212.4(4)	1870.1(6)
Space group	$C2/c$	$P2_1/n$	$P\bar{1}$
Z	8	4	2
μ(Mo-Kα)/mm^{-1}	1.584	1.85	2.607
Meas. refl.	7475	9445	18374
Ind. refl.	2046	2315	6811
R_{int}	0.0736	0.0484	0.0637
$R_1(F)$ ($I > 2\sigma(I)$)	0.0446	0.0382	0.0424
$wR_2(F^2)$ (all data)	0.1192	0.0985	0.0940

Crystallography †

Details about data collection and refinement are given in Table 3. Data were collected on a STOE-IPDS imaging plate system at 293 K. Numerical absorption corrections were applied for the three structures. The hydrogen atom was introduced at calculated position in **5**, they were not introduced in **4** and [**9**]$_3$[Mo_6Cl_{14}] where the ethylene bridges are disordered.

† CCDC reference numbers 172092. See http://www.rsc.org/suppdata/p1/b1/b106144p/ for crystallographic files in .cif or other electronic format.

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