S⋯S and S⋯P chalcogen bonding in solution: A cryospectroscopic study of the complexes of 2,2,4,4-tetrafluoro-1,3-dithietane with dimethyl sulfide and trimethylphosphine.

Yannick Geboes,[a] Elias De Vos,[a] and Wouter A. Herrebout[a]*

[a] Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp (Belgium), E-mail: wouter.herrebout@uantwerpen.be

Electronic supplementary information

Table S1.1: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of 2,2,4,4-Tetrafluoro-1,3-dithiethane ($C_2F_4S_2$).

D_{2h}	X	Y	Z
$C_2F_4S_2$			
S	0.000000	1.387164	0.000000
C	1.191095	0.000000	0.000000
F	2.014655	0.000000	1.085309
F	2.014655	0.000000	-1.085309
S	0.000000	-1.387164	0.000000
C	-1.191095	0.000000	0.000000
F	-2.014655	0.000000	1.085309
F	-2.014655	0.000000	-1.085309

Table S1.2: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of TMP.

C_{3v}	X	Y	Z
TMP			
P	0.000000	0.000000	0.618978
C	0.000000	1.626598	-0.285498
H	-0.889964	2.208825	-0.001487
H	0.889964	2.208825	-0.001487
H	0.000000	1.481355	-1.378927
C	-1.408675	-0.813299	-0.285498
H	-1.467917	-1.875144	-0.001487
H	-2.357881	-0.333681	-0.001487
H	-1.282891	-0.740678	-1.378927
C	1.408675	-0.813299	-0.285498
H	2.357881	-0.333681	-0.001487
H	1.467917	-1.875144	-0.001487
H	1.282891	-0.740678	-1.378927

Table S1.3: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of DMS.

C_{2v}	X	Y	Z
DMS			
S	0.000000	0.674247	0.000000
C	-1.370330	-0.522675	0.000000
H	-2.309643	0.047454	0.000000
H	-1.334542	-1.152689	-0.900834
H	-1.334542	-1.152688	0.900834
C	1.370330	-0.522675	0.000000
H	1.334542	-1.152689	-0.900834
H	2.309643	0.047454	0.000000
H	1.334542	-1.152689	0.900834

Table S2.1: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of the chalcogen bonded complex between $C_2F_4S_2$ and dimethyl sulfide at the global minimum.

C_s	X	Y	Z
$C_2F_4S_2$			
S	0.191356	-0.733470	-0.170850
C	1.998971	-0.804876	0.120000
F	2.675866	-1.503257	-0.838102
F	2.334294	-1.398324	1.303986
S	2.355308	0.986928	0.089336
C	0.548378	1.061456	-0.190256
F	0.218467	1.672270	-1.359591
F	-0.104439	1.757456	0.786727
DMS			
S	-2.859015	0.181457	-0.363551
C	-3.235859	-1.581365	-0.605585
H	-4.248327	-1.810630	-0.243224
H	-3.182924	-1.788818	-1.683338
H	-2.498517	-2.208496	-0.080780
C	-2.998860	0.219438	1.450564
H	-2.265451	-0.463617	1.904766
H	-2.782994	1.245794	1.777093
H	-4.017638	-0.054091	1.761016

Table S2.2: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of the chalcogen bonded complex between $C_2F_4S_2$ and dimethyl sulfide at the local minimum.

C_s	X	Y	Z
$C_2F_4S_2$			
S	0.483353	-0.877370	-0.433442
C	2.251251	-0.541287	-0.092591
F	3.053797	-0.702704	-1.184430
F	2.782383	-1.350728	0.870443
S	2.105149	1.202043	0.438060
C	0.337593	0.856257	0.124666
F	-0.209630	1.690191	-0.804410
F	-0.432023	1.008326	1.245986
DMS			
S	-2.792931	-0.675882	-0.586140
C	-3.024137	-1.291501	1.111104
H	-4.092611	-1.309448	1.370344
H	-2.628175	-2.315927	1.148773
H	-2.469421	-0.664377	1.823782
C	-3.475305	0.994150	-0.348929
H	-2.909878	1.532429	0.424861
H	-3.377866	1.529499	-1.303355
H	-4.538355	0.935700	-0.073858

Table S2.3: Cartesian coordinates of the MP2/aug-cc-pVDZ optimized geometry of the chalcogen bonded complex between $C_2F_4S_2$ and trimethylphosphine.

C_s	X	Y	Z
$C_2F_4S_2$			
S	-0.746085	-0.943557	-0.171824
C	-0.732578	0.878359	-0.018044
F	-0.185704	1.519432	-1.090931
F	-0.036342	1.334175	1.068263
S	-2.531490	1.164174	0.132565
C	-2.550666	-0.657026	-0.024279
F	-3.261768	-1.093164	-1.105756
F	-3.113856	-1.280533	1.052831
TMP			
P	2.558113	-0.347296	-0.089767
C	3.200323	1.336227	-0.535494
H	3.088853	1.499781	-1.618090
H	2.609212	2.103553	-0.013508
H	4.262389	1.446135	-0.259685
C	3.884403	-1.394855	-0.860612
H	3.746514	-2.445621	-0.563728
H	3.809639	-1.338031	-1.957123
H	4.889070	-1.062438	-0.550509
C	3.103800	-0.418643	1.683307
H	2.500793	0.283101	2.279263
H	2.939954	-1.431734	2.081225
H	4.170424	-0.158729	1.787862

Table S3: MP2/aug-cc-pVDZ ΔE(DZ) and CCSD(T)/CBS extrapolated complexation energies ΔE(CCSD(T)), calculated vapor phase complexation enthalpies $\Delta H°$ (vap,calc), the calculated complexation enthalpies in liquid krypton ($\Delta H°$ (LKr,calc)) and the corresponding experimentally obtained complexation enthalpy ($\Delta H°$ (LKr)) (kJ mol^{-1}) of the chalcogen bonded complexes between $C_2F_4S_2$ and dimethyl ether. All data are taken from Reference 36.

	S···O Chalcogen bonded complexes	
	Global Minimum	Local Minimum
ΔE (DZ)	-23.4	-22.2
ΔE (CCSD(T))	-25.0	-23.5
$\Delta H°$ (vap,calc)	-22.1	-20.8
$\Delta H°$ (LKr,calc)	-16.6	-15.2
Experimental		
$\Delta H°$ (LKr)	-13.5(1)	

Table S4: MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman intensities, in Å^4 amu^{-1}, for the chalcogen bonded complex between $C_2F_4S_2$ and DMS and both monomers, as well as the complexation shift Δv.

	Monomer			Chalcogen bonded complex, global minimum			
	Frequency	IR int.	Raman int.	Frequency	Δv	IR int.	Raman int.
$C_2F_4S_2$							
v_1 (A$_g$)	1160.9	0.0	8.6	1157.0	-4.0	5.4	7.7
v_2 (A$_g$)	651.0	0.0	15.5	648.1	-2.8	1.0	20.3
v_3 (A$_g$)	513.3	0.0	14.7	512.0	-1.4	1.4	33.7
v_4 (A$_g$)	323.4	0.0	3.0	323.9	0.5	0.4	3.0
v_5 (A$_u$)	231.2	0.0	0.0	235.0	3.8	0.03	0.004
v_6 (B$_{1g}$)	839.9	0.0	8.4	835.7	-4.3	6.4	22.4
v_7 (B$_{1g}$)	422.6	0.0	5.3	424.3	1.7	1.4	14.9
v_8 (B$_{1u}$)	1095.1	320.6	0.0	1088.9	-6.2	277.2	0.2
v_9 (B$_{1u}$)	428.3	0.4	0.0	430.0	1.7	0.3	0.0
v_{10} (B$_{1u}$)	56.3	1.2	0.0	60.0	3.7	1.0	0.1
v_{11} (B$_{2g}$)	1079.3	0.0	4.9	1073.8	-5.5	106.5	3.4
v_{12} (B$_{2g}$)	377.9	0.0	1.3	381.8	3.9	0.0	1.2
v_{13} (B$_{2u}$)	970.0	128.0	0.0	964.7	-5.3	139.1	5.8
v_{14} (B$_{2u}$)	335.3	4.5	0.0	335.8	0.6	8.9	1.8
v_{15} (B$_{3g}$)	282.2	0.0	2.1	286.6	4.4	0.0008	1.9
v_{16} (B$_{3u}$)	1065.2	732.2	0.0	1059.3	-5.9	562.2	3.9
v_{17} (B$_{3u}$)	638.7	15.9	0.0	636.3	-2.4	8.8	5.2
v_{18} (B$_{3u}$)	445.4	2.1	0.0	444.5	-0.9	5.7	3.6
DMS							
v_1 (A$_1$)	3186.3	9.8	92.1	3188.4	2.0	4.6	73.2
v_2 (A$_1$)	3062.2	31.8	338.0	3059.6	-2.6	26.2	273.4
v_3 (A$_1$)	1473.5	0.3	7.6	1471.0	-2.5	2.9	9.1
v_4 (A$_1$)	1352.5	0.8	0.9	1351.6	-0.9	0.1	7.6
v_5 (A$_1$)	1046.4	8.6	0.4	1047.0	0.6	10.3	0.6
v_6 (A$_1$)	713.3	2.8	22.1	711.6	-1.7	3.4	17.4
v_7 (A$_1$)	260.8	0.03	3.0	262.6	1.8	0.07	2.5
v_8 (A$_2$)	3168.0	0.0	16.5	3168.1	0.0	1.9	27.9
v_9 (A$_2$)	1450.1	0.0	10.3	1447.6	-2.5	0.2	9.1
v_{10} (A$_2$)	945.6	0.0	0.1	948.8	3.2	0.007	0.5
v_{11} (A$_2$)	171.2	0.0	0.1	174.8	3.6	0.04	0.2
v_{12} (B$_1$)	3159.9	21.3	119.4	3159.5	-0.4	18.9	107.3
v_{13} (B$_1$)	1462.5	12.9	0.02	1460.2	-2.3	12.2	0.6
v_{14} (B$_1$)	982.7	4.1	0.006	984.8	2.1	8.6	0.8
v_{15} (B$_1$)	187.1	0.8	0.09	192.0	4.9	2.1	0.5
v_{16} (B$_2$)	3187.4	3.4	42.0	3192.5	5.1	2.8	44.8
v_{17} (B$_2$)	3066.9	26.3	2.8	3065.3	-1.6	18.9	45.3
v_{18} (B$_2$)	1464.2	13.6	0.03	1461.2	-3.0	10.5	0.4
v_{19} (B$_2$)	1326.0	6.5	0.1	1325.5	-0.4	3.4	0.2
v_{20} (B$_2$)	912.7	0.2	0.2	915.1	2.4	0.2	0.2
v_{21} (B$_2$)	765.1	0.1	8.5	763.1	-1.9	0.5	6.9

Van der Waals vibrations: 22.3 cm^{-1}, 0.8 km mol^{-1}, 0.5 Å^4 amu^{-1}, 40.4 cm^{-1}, 0.7 km mol^{-1}, 0.4 Å^4 amu^{-1}, 53.6 cm^{-1}, 0.1 km mol^{-1}, 0.3 Å^4 amu^{-1}, 71.7 cm^{-1}, 1.2 km mol^{-1}, 1.5 Å^4 amu^{-1}, 89.6 cm^{-1}, 0.03 km mol^{-1}, 1.4 Å^4 amu^{-1}, 122.3 cm^{-1}, 11.2 km mol^{-1}, 4.6 Å^4 amu^{-1}.

Table S5: MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman intensities, in Å^4 amu^{-1}, for the chalcogen bonded complex between $C_2F_4S_2$ and DMS and both monomers, as well as the complexation shift Δv.

	Monomer			Chalcogen bonded complex, local minimum			
	Frequency	IR int.	Raman int.	Frequency	Δv	IR int.	Raman int.
$C_2F_4S_2$							
v_1 (A$_g$)	1160.9	0.0	8.6	1155.4	-5.5	6.6	6.8
v_2 (A$_g$)	651.0	0.0	15.5	647.7	-3.3	0.7	20.6
v_3 (A$_g$)	513.3	0.0	14.7	512.5	-0.8	0.8	27.6
v_4 (A$_g$)	323.4	0.0	3.0	324.5	1.1	0.4	3.5
v_5 (A$_u$)	231.2	0.0	0.0	235.6	4.4	0.03	0.02
v_6 (B$_{1g}$)	839.9	0.0	8.4	837.8	-2.2	6.2	23.3
v_7 (B$_{1g}$)	422.6	0.0	5.3	423.9	1.3	0.8	13.5
v_8 (B$_{1u}$)	1095.1	320.6	0.0	1084.0	-11.1	274.8	0.4
v_9 (B$_{1u}$)	428.3	0.4	0.0	430.1	1.8	0.4	0.02
v_{10} (B$_{1u}$)	56.3	1.2	0.0	64.7	8.4	1.1	0.06
v_{11} (B$_{2g}$)	1079.3	0.0	4.9	1069.6	-9.7	161.7	3.3
v_{12} (B$_{2g}$)	377.9	0.0	1.3	381.8	3.9	0.07	1.1
v_{13} (B$_{2u}$)	970.0	128.0	0.0	966.7	-3.3	133.4	2.9
v_{14} (B$_{2u}$)	335.3	4.5	0.0	335.9	0.7	8.1	0.9
v_{15} (B$_{3g}$)	282.2	0.0	2.1	286.4	4.2	0.006	1.8
v_{16} (B$_{3u}$)	1065.2	732.2	0.0	1055.6	-9.7	542.8	3.3
v_{17} (B$_{3u}$)	638.7	15.9	0.0	636.4	-2.3	9.6	3.4
v_{18} (B$_{3u}$)	445.4	2.1	0.0	444.9	-0.5	6.0	2.4
DMS							
v_1 (A$_1$)	3186.3	9.8	92.1	3188.3	2.0	5.3	57.8
v_2 (A$_1$)	3062.2	31.8	338.0	3066.4	4.2	26.0	305.9
v_3 (A$_1$)	1473.5	0.3	7.6	1472.5	-1.0	1.7	7.8
v_4 (A$_1$)	1352.5	0.8	0.9	1351.7	-0.8	0.9	4.9
v_5 (A$_1$)	1046.4	8.6	0.4	1046.9	0.6	15.6	0.9
v_6 (A$_1$)	713.3	2.8	22.1	710.8	-2.5	3.8	19.0
v_7 (A$_1$)	260.8	0.03	3.0	261.6	0.8	0.02	2.5
v_8 (A$_2$)	3168.0	0.0	16.5	3176.4	8.4	0.3	18.7
v_9 (A$_2$)	1450.1	0.0	10.3	1448.3	-1.8	0.4	9.5
v_{10} (A$_2$)	945.6	0.0	0.1	948.7	3.1	0.07	0.4
v_{11} (A$_2$)	171.2	0.0	0.1	172.9	1.7	0.1	0.2
v_{12} (B$_1$)	3159.9	21.3	119.4	3169.4	9.5	14.5	121.5
v_{13} (B$_1$)	1462.5	12.9	0.02	1461.0	-1.6	14.1	0.3
v_{14} (B$_1$)	982.7	4.1	0.006	985.6	3.0	14.0	0.04
v_{15} (B$_1$)	187.1	0.8	0.09	186.0	-1.1	1.5	0.4
v_{16} (B$_2$)	3187.4	3.4	42.0	3192.0	4.6	3.2	49.3
v_{17} (B$_2$)	3066.9	26.3	2.8	3071.1	4.2	20.4	28.3
v_{18} (B$_2$)	1464.2	13.6	0.03	1462.5	-1.6	10.0	0.1
v_{19} (B$_2$)	1326.0	6.5	0.1	1325.1	-0.9	4.1	0.2
v_{20} (B$_2$)	912.7	0.2	0.2	915.3	2.5	0.2	0.3
v_{21} (B$_2$)	765.1	0.1	8.5	763.4	-1.7	0.5	7.3

Van der Waals vibrations: 23.2 cm^{-1}, 0.5 km mol^{-1}, 0.2 Å^4 amu^{-1}, 44.7 cm^{-1}, 0.1 km mol^{-1}, 0.8 Å^4 amu^{-1}, 61.9 cm^{-1}, 1.1 km mol^{-1}, 0.9 Å^4 amu^{-1}, 71.2 cm^{-1}, 0.5 km mol^{-1}, 1.0 Å^4 amu^{-1}, 83.0 cm^{-1}, 0.6 km mol^{-1}, 1.5 Å^4 amu^{-1}, 103.9 cm^{-1}, 7.9 km mol^{-1}, 1.5 Å^4 amu^{-1}.

Table S6: MP2/aug-cc-pVDZ vibrational frequencies, in cm^{-1}, infrared intensities, in km mol^{-1}, and Raman intensities, in Å^4 amu^{-1}, for the chalcogen bonded complex between $C_2F_4S_2$ and TMP and both monomers, as well as the complexation shift Δv.

	Monomer			Chalcogen bonded complex			
	Frequency	IR int.	Raman int.	Frequency	Δv	IR int.	Raman int.
$C_2F_4S_2$							
v_1 (A_g)	1160.9	0.0	8.6	1153.5	-7.4	6.9	7.1
v_2 (A_g)	651.0	0.0	15.5	646.6	-4.3	1.5	23.7
v_3 (A_g)	513.3	0.0	14.7	511.2	-2.1	1.2	37.4
v_4 (A_g)	323.4	0.0	3.0	323.9	0.5	0.8	4.5
v_5 (A_u)	231.2	0.0	0.0	235.5	4.3	0.04	0.04
v_6 (B_{1g})	839.9	0.0	8.4	836.8	-3.1	10.2	31.7
v_7 (B_{1g})	422.6	0.0	5.3	423.5	0.9	1.2	19.2
v_8 (B_{1u})	1095.1	320.6	0.0	1081.6	-13.6	275.2	0.4
v_9 (B_{1u})	428.3	0.4	0.0	429.8	1.5	0.3	0.0
v_{10} (B_{1u})	56.3	1.2	0.0	60.8	4.5	0.9	0.1
v_{11} (B_{2g})	1079.3	0.0	4.9	1065.7	-13.6	120.1	4.6
v_{12} (B_{2g})	377.9	0.0	1.3	381.8	3.9	0.1	0.9
v_{13} (B_{2u})	970.0	128.0	0.0	966.8	-3.2	84.8	20.3
v_{14} (B_{2u})	335.3	4.5	0.0	334.9	-0.4	9.6	2.2
v_{15} (B_{3g})	282.2	0.0	2.1	286.6	4.4	0.009	1.8
v_{16} (B_{3u})	1065.2	732.2	0.0	1054.9	-10.4	594.9	8.1
v_{17} (B_{3u})	638.7	15.9	0.0	635.2	-3.5	8.1	7.5
v_{18} (B_{3u})	445.4	2.1	0.0	444.0	-1.4	7.3	4.8
TMP							
v_1 (A_1)	3148.5	33.6	160.8	3152.0	3.5	26.9	175.0
v_2 (A_1)	3043.5	29.4	528.4	3046.7	3.1	38.5	556.7
v_3 (A_1)	1469.0	9.2	1.5	1467.7	-1.3	7.5	1.4
v_4 (A_1)	1314.7	5.1	7.3	1315.0	0.3	3.2	14.3
v_5 (A_1)	957.8	20.1	5.0	957.2	-0.7	106.2	13.9
v_6 (A_1)	660.9	0.5	26.5	662.8	1.9	0.7	25.5
v_7 (A_1)	287.5	1.0	1.5	287.2	-0.4	1.3	1.2
v_8 (A_2)	3168.1	0.0	0.0	3171.1	3.0	2.9	30.0
v_9 (A_2)	1440.1	0.0	0.0	1439.0	-1.1	0.02	0.2
v_{10} (A_2)	776.6	0.0	0.0	779.8	3.2	0.002	0.006
v_{11} (A_2)	164.1	0.0	0.0	164.7	0.6	0.002	0.008
v_{12} (E)	3167.9	11.5	95.9	3172.3	4.4	6.5	63.1
v_{13} (E)	3149.3	3.0	18.4	3153.5	4.2	4.4	35.6
v_{14} (E)	3046.9	16.7	4.2	3050.0	3.1	12.9	16.8
v_{15} (E)	1456.7	8.7	3.0	1455.6	-1.1	8.5	3.6
v_{16} (E)	1446.2	3.1	9.5	1445.0	-1.2	2.2	8.4
v_{17} (E)	1290.0	2.3	0.7	1290.4	0.5	3.1	0.6
v_{18} (E)	946.6	16.5	0.5	949.0	2.5	14.0	0.5
v_{19} (E)	831.0	0.2	0.3	832.7	1.8	0.6	1.9
v_{20} (E)	718.3	11.6	11.8	725.3	7.0	9.2	12.6
v_{21} (E)	249.8	0.2	2.8	246.3	-3.5	0.3	2.5
v_{22} (E)	207.4	0.0009	0.6	207.3	0.0	0.004	0.4

Van der Waals vibrations: 16.5 cm^{-1}, 0.05 km mol^{-1}, 0.2 Å^4 amu^{-1}, 24.6 cm^{-1}, 0.3 km mol^{-1}, 0.4 Å^4 amu^{-1}, 39.3 cm^{-1}, 1.4 km mol^{-1}, 0.6 Å^4 amu^{-1}, 59.4 cm^{-1}, 0.6 km mol^{-1}, 2.0 Å^4 amu^{-1}, 72.7 cm^{-1}, 0.2 km mol^{-1}, 0.5 Å^4 amu^{-1}, 80.0 cm^{-1}, 0.1 km mol^{-1}, 1.9 Å^4 amu^{-1}.

Table S7: Overview of the different van 't Hoff plots constructed for the chalcogen bonded complex between $C_2F_4S_2$ and DME in LKr in the 121-155 K temperature interval, showing the estimated mole fractions of each monomer, range of the integrated monomer and complex bands and complex enthalpies $\Delta H°$ (LKr).

$x_{C_2F_4S_2}$	x_{DMS}	Integrated $C_2F_4S_2$ band (cm^{-1})	Integrated DMS band (cm^{-1})	Integrated Complex band (cm^{-1})	$\Delta H°$ (LKr) [a]
9.4×10^{-5}	1.9×10^{-3}	1125-1058	1345-1290	1073.2-1055	-12.97(8)
9.4×10^{-5}	1.9×10^{-3}	970.5-950.3	1080-945	965-950	-12.4(1)
3.8×10^{-5}	1.4×10^{-3}	1125-1096.7	998-952	1073-1055	-12.0(1)
3.8×10^{-5}	1.4×10^{-3}	973-950.5	1053-1006	962-953.5	-12.5(1)
1.9×10^{-3}	1.1×10^{-3}	968.5-952	1065-1002	963.5-952	-12.5(3)
1.9×10^{-4}	5.6×10^{-4}	1127-1096.8	1480-1395	966-951	-11.7(2)
1.9×10^{-4}	5.6×10^{-4}	974-950.2	3025-2815	1111-1094.5	-12.00(4)

[a] Values are given with the standard deviation of the linear regression in parentheses.


Table S8: Overview of the different van 't Hoff plots constructed for the chalcogen bonded complex between $C_2F_4S_2$ and TMP in LKr in the 121-155 K temperature interval, showing the estimated mole fractions of each monomer, range of the integrated monomer and complex bands and complex enthalpies $\Delta H°$ (LKr).

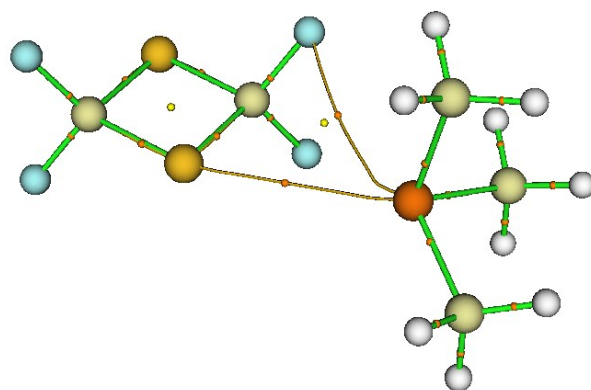| $x_{C_2F_4S_2}$	x_{DMS}	Integrated $C_2F_4S_2$ band (cm^{-1})	Integrated TMP band (cm^{-1})	Integrated Complex band (cm^{-1})	$\Delta H°$ (LKr) [a]
1.9×10^{-4}	1.9×10^{-3}	1122-1096.5	3010-2930.5	964-943.4	-13.1(1)
2.8×10^{-5}	1.1×10^{-3}	970-952	3010-2930.5	1120-1040	-12.85(5)
9.4×10^{-5}	1.0×10^{-3}	1127-1096.8	3010-2930.5	1112-1076.8	-12.73(4)
9.4×10^{-5}	1.0×10^{-3}	970-952	1460-1400	963-943	-12.96(6)
1.9×10^{-5}	1.1×10^{-3}	1127-1096.8	1330-1260	1112.5-1051.7	-12.54(8)
3.8×10^{-4}	5.6×10^{-4}	659.7-644.1	1460-1400	1441-1413	-13.82(5)

[a] Values are given with the standard deviation of the linear regression in parentheses.
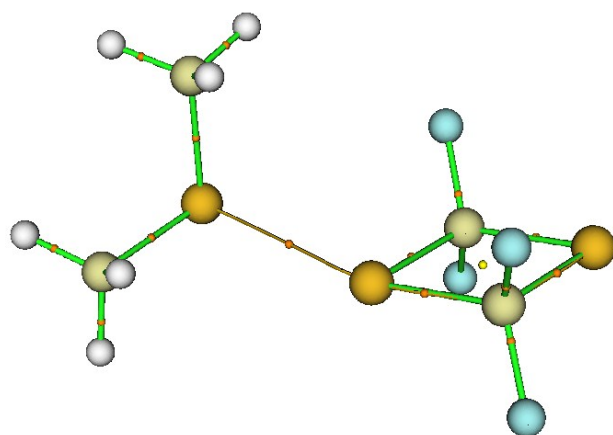
electron densities, in a.u., at the bond critical point :   S···S 0.0155
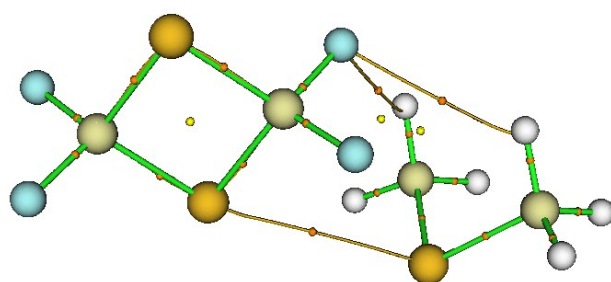
electron densities, in a.u., at the bond critical points :   S···S 0.0129
                                                                                    F…H 0.0046
                                                                                   F…H 0.0051

electron densities, in a.u., at the bond critical points :   S···P 0.0131
                                                                                    F···P 0.0068

Figure S1. Bond critical points (orange), ring critical points (yellow) and bond paths for the complexes of $C_2F_4S_2$ with dimethyl sulfide and trimethylphosphine. All results are obtained using the MP2/aug-cc-pVDZ electron density.
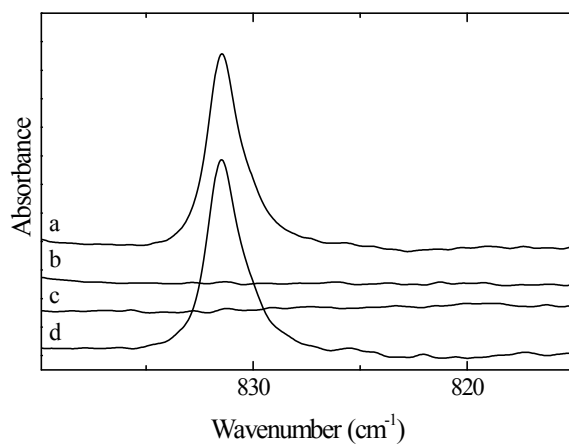
Figure S2: Infrared spectra of the $C_2F_4S_2$ ν_6 spectral region for the mixtures of $C_2F_4S_2$ with TMP-d_9 dissolved in LKr at 133 K. In each panel, trace *a* represents the mixed solution, while traces *b* and *c* show the rescaled spectra of the solutions containing only $C_2F_4S_2$ or TMP-d_9, respectively. Trace *d* represents the spectrum of the complex which is obtained by subtracting the rescaled traces *b* and *c* from trace *a*. Estimated mole fractions of the solutions of the mixture are 3.8×10^{-4} for $C_2F_4S_2$ and 9.4×10^{-4} for TMP-d_9.