Supplementary Information (SI) for Dalton Transactions.

Chalcogen Bonding vs. Weakly Coordinating Anions – A Solid State Study on Halidoselenium Cations in an Oxoanionic Environment.

Jan Langwald,[a] Sergi Burguera,[b] Antonio Frontera *[b] and Mathias S. Wickleder*[a]

[a] *Institute of Inorganic and Materials Chemistry, University of Cologne, Greinstr. 6, 50939 Cologne, Germany. E-mail: mathias.wickleder@uni-koeln.de*

[b] *Universitat de les Illes Balears, Crta de Valldemossa km 7.5, 07122 Palma de Mallorca, Baleares, Spain. E-mail: toni.frontera@uib.es*

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A. Synthesis

General Procedure

SO_3 was obtained in a specially designed apparatus for the generation, distillation and the subsequent transfer into glass ampoules under nitrogen gas. For this purpose, fuming sulfuric acid (5 mL, 65% SO_3, used as received, Merck, Darmstadt, Germany) was added via a dropping funnel into a 500 mL flask with P_4O_{10} (250 g, >97%, Merck, Darmstadt) with a dosage rate of 1 mL / minute. At the same time, the flask was heated at 130 °C and the generated SO_3 distilled into a connected burette body (scaling 0.01 ml). A connected glass ampoule (l = 200 mm, ø = 16 mm, thickness of the tube wall = 1.80 mm) containing the solid starting materials was then filled with the required amount of SO_3.

Selenoyl chloride ($SeOCl_2$) was prepared according to literature procedures and it's purity confirmed *via* ^{77}Se NMR spectroscopy ([$CDCl_3$]:1496 ppm, s).[1-2]

Synthesis of $[SeCl_3]_2[S_2O_7]$ (1)

64.3 mg (2.01 mmol, 1.00 eq.) of Sulfur powder (reagent grade, Sigma Aldrich) and 0.20 mL (2.93 mmol, 1.46 eq.) of Selenoyl chloride were filled into a preheated glass ampoule (3.3 borosilicate). 0.20 mL SO_3 (5.00 mmol, 2.49 eq.) were condensed on top and the ampoule was sealed under reduced pressure ($1\cdot10^{-3}$ mbar) with a gas burner. The reaction vessel was heated to 80 °C within 24 h, dwelled at this temperature for 48 h and cooled down to room temperature (in the following 'r.t.') within 90 h. After cooling, few colourless crystals could be isolated besides amorphous byproducts.

Synthesis of $[SeCl_3][ClSO_3]$ (3)

65.5 mg (2.04 mmol, 1.00 eq.) of Sulfur powder (reagent grade, Sigma Aldrich) and 0.20 mL (2.93 mmol, 1.46 eq.) of Selenoyl chloride were filled into a preheated glass ampoule (3.3 borosilicate). 0.20 mL SO_3 (5.00 mmol, 2.45 eq.) were condensed on top and the ampoule was sealed under reduced pressure ($1\cdot10^{-3}$ mbar) with a gas burner. From the resulting red/orange solid slurry, few colourless crystals could be isolated.

Synthesis of $[Se_2I_4]_2[S_4O_{13}]_2(SO_3)$ (4)

83.4 mg (1.06 mmol, 1.00 eq.) of Selenium powder (99+%, ACROS Organics) and 200.8 mg (0.79 mmol, 0.75 eq.) of Iodine (Riedel-de Haën, Seelze) were filled into a preheated glass ampoule (3.3 borosilicate). 0.20 mL SO_3 (5.00 mmol, 4.73 eq.) were condensed on top and the ampoule was sealed under reduced pressure ($1\cdot10^{-3}$ mbar) with a gas burner. The reaction vessel was heated to 80 °C within 24 h, dwelled at this temperature for 48 h and cooled down to r.t. within 90 h. After cooling, few dark red-violet crystals could be isolated from the dark violet mother liquid.

B. Structure Determination and Crystallographic Details

General Procedure

The single crystal structure determination was performed on a *Bruker D8 VENTURE KAPPA* diffractometer with a microfocus sealed tube using a multilayer mirror as the monochromator and a *Bruker PHOTON III* detector. As characteristic X-ray radiation MoK_{α} ($\lambda = 71.073$ pm) or AgK_{α} ($\lambda = 56.086$ pm) was used for the measurements. Before the measurements, the crystals were prepared in perfluorinated ether oil (Fomblin® YR-180) and selected using a light microscope with equipped polarization filter. A suitable single crystal was fixed on a MiTeGen micromount (150 µm polymer loop) and adjusted to the X-ray beam and cooled down to 100 K in a stream of N_2. The images with the intensity data were processed using the software *APEX5*.[3] The frames were integrated with the Bruker *SAINT* software package using a narrow frame algorithm. Absorption effects were corrected using SADABS for the multi-scan absorption correction.[4-5] The structure solution and refinement were done with the software *OLEX2*.[6] Dual methods using *SHELXT* were used for structure solution and full-matrix least-squares methods against F^2 using *SHELXL* for the refinement.[7-8] All illustrations of the crystal structures were made with the program *Diamond 4* using the .cif as the input file.[9]

$SeOCl_2$

Table S1: Crystallographic data of $SeOCl_2$

Empirical formula	Cl_2OSe
Formula weight	165.86 g/mol
Temperature	100.00 K
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell dimensions	a = 1961.48(9) pm
	b = 438.52(2) pm
	c = 2818.9(1) pm
	β = 98.249(2)°
Volume	2399.6(2) $Å^3$
Z	24
ρ_{calc}	2.755 g/cm^3
μ	10.500 mm^{-1}
F(000)	1824
Crystal size	0.65 × 0.23 × 0.1 mm^3
Radiation	MoK_α (λ = 0.71073 nm)
2Θ range for data collection	5.446 to 57.398
Index ranges	$-26 \leq h \leq 26$, $-5 \leq k \leq 4$, $-38 \leq l \leq 38$
Reflections collected	39501
Independent reflections	6087 [R_{int} = 0.0335, R_σ = 0.0228]
Completeness	98.1%
Absorption correction	multiscan
Min. and max. transmission	0.301 / 0.747
Data/restraints/parameters	6087/0/217
Goodness-of-fit on F^2	1.079
Final R indexes [$I \geq 2\sigma$ (I)]	R_1 = 0.0341, wR_2 = 0.0713
Final R indexes [all data]	R_1 = 0.0447, wR_2 = 0.0761
Largest diff. peak/hole	0.97/–0.68 $e \cdot Å^{-3}$
CCDC-No.	2516864

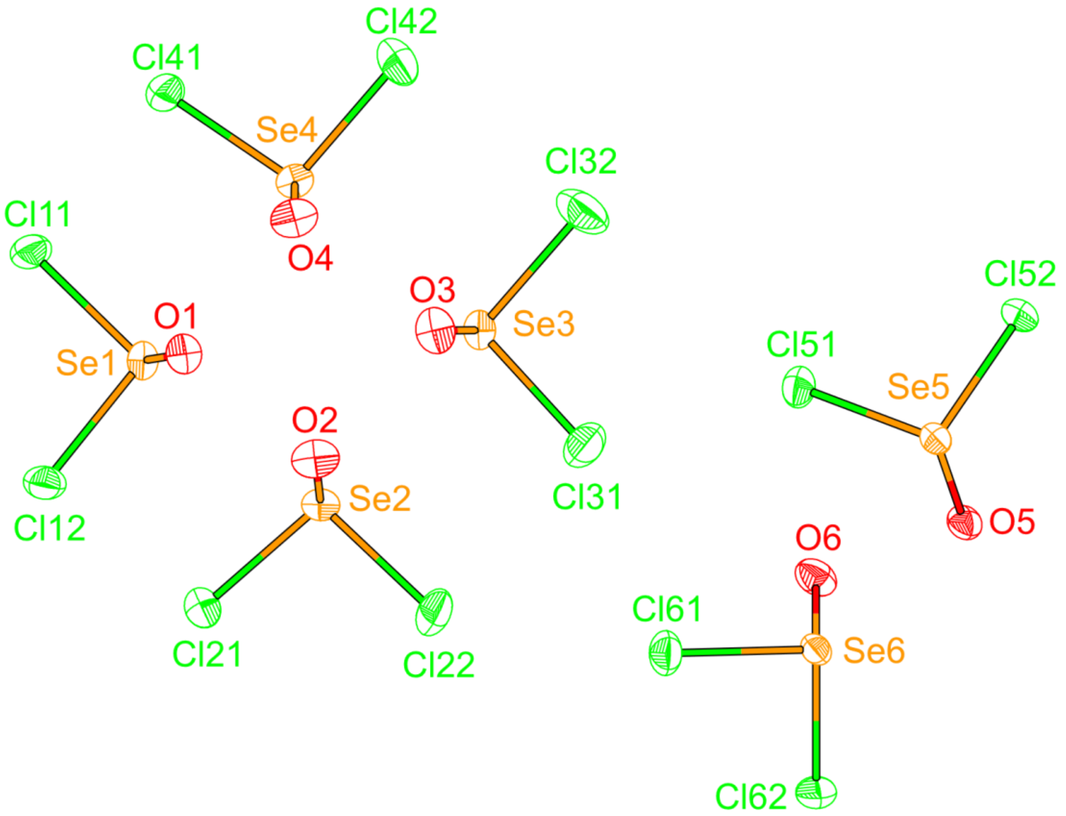

Figure S1: Thermal ellipsoid plot of the asymmetric unit of $SeOCl_2$ shown with 50% probability.

Table S2: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $SeOCl_2$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Se1	1369.6(2)	2326.2(8)	5493.3(2)	20.01(9)
Cl11	707.8(6)	2317(3)	4808.2(4)	36.0(3)
Cl12	535.8(6)	2442(3)	5926.6(4)	35.0(2)
O1	1681.3(14)	5745(6)	5538.5(10)	23.4(6)
Se2	2476.2(2)	7360.4(8)	6468.6(2)	20.84(9)
Cl21	1522.9(6)	7313(3)	6778.4(4)	35.6(2)
Cl22	3151.0(6)	7592(4)	7150.2(4)	46.0(3)
O2	2507.0(17)	10766(6)	6257.8(11)	29.4(7)
Se3	3779.2(2)	2372.3(8)	5856.9(2)	21.51(9)
Cl31	4385.5(7)	2318(3)	6562.1(4)	41.8(3)
Cl32	4644.8(7)	2472(4)	5451.5(5)	52.8(4)
O3	3481.5(15)	5810(7)	5807.5(12)	29.8(7)
Se4	2671.3(2)	7316.1(8)	4893.5(2)	20.92(9)
Cl41	1861.1(6)	7165(3)	4278.1(4)	32.7(2)
Cl42	3534.5(6)	7406(3)	4484.0(5)	45.6(3)
O4	2638.6(17)	10779(6)	5083.5(10)	28.6(6)
Se5	6853.3(2)	-662.3(9)	7048.4(2)	20.28(9)
Cl51	5942.8(5)	-2396(3)	6588.2(4)	34.4(2)
Cl52	7584.5(5)	-2297(3)	6581.9(4)	30.0(2)
O5	6949.2(14)	-3108(7)	7478.7(10)	24.9(6)
Se6	5788.0(2)	4551.2(9)	7889.5(2)	20.87(9)
Cl61	4730.2(5)	6090(3)	7686.4(4)	34.2(2)
Cl62	5611.7(6)	2295(3)	8557.9(4)	33.8(2)
O6	5858.5(16)	1761(7)	7536.1(11)	30.9(7)

Table S3: Anisotropic Displacement Parameters (Å^2×10^3) for $SeOCl_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Se1	19.46(17)	11.19(16)	28.6(2)	-0.64(14)	0.67(15)	-0.88(14)
Cl11	35.1(6)	51.1(7)	21.5(5)	-4.3(5)	2.4(4)	-13.7(5)
Cl12	35.4(5)	46.7(7)	24.4(5)	-2.3(5)	9.1(4)	-12.5(5)
O1	25.4(14)	12.9(12)	31.8(15)	-1.1(11)	3.4(12)	-2.9(11)
Se2	29.3(2)	12.54(17)	21.38(18)	0.89(14)	6.00(15)	2.84(15)
Cl21	25.6(5)	47.6(7)	34.2(5)	-2.8(5)	6.1(4)	-0.9(5)
Cl22	30.7(6)	66.2(9)	37.3(6)	12.1(6)	-8.4(5)	1.9(6)
O2	46.2(18)	12.6(13)	29.7(15)	2.0(11)	7.2(13)	1.3(13)
Se3	21.08(18)	12.63(17)	30.2(2)	-1.98(15)	1.56(15)	1.18(14)
Cl31	39.6(6)	49.8(7)	32.5(6)	-1.7(5)	-6.4(5)	4.6(6)
Cl32	48.5(7)	62.4(9)	54.1(8)	6.8(7)	29.5(6)	16.1(7)
O3	31.0(16)	14.8(14)	43.6(18)	0.5(13)	5.3(13)	4.1(12)
Se4	28.7(2)	11.93(17)	21.96(18)	-1.14(14)	2.93(15)	0.24(15)
Cl41	30.4(5)	40.5(6)	26.4(5)	-2.3(4)	1.5(4)	-6.0(5)
Cl42	29.9(6)	58.3(8)	51.2(7)	-2.9(6)	14.6(5)	2.8(6)
O4	45.3(18)	11.5(13)	28.8(15)	-4.4(11)	4.7(13)	-1.5(12)
Se5	19.10(18)	20.62(18)	21.92(18)	0.94(15)	5.68(14)	0.90(15)
Cl51	22.5(5)	47.2(7)	32.3(5)	-7.5(5)	-0.6(4)	-1.7(5)
Cl52	25.2(5)	41.3(6)	25.3(5)	-4.3(4)	9.8(4)	2.7(4)
O5	23.3(14)	26.1(14)	26.2(14)	6.5(12)	7.0(11)	-0.6(12)
Se6	17.66(17)	24.04(19)	21.81(18)	-1.68(15)	5.89(14)	-1.92(15)
Cl61	21.9(5)	40.0(6)	39.3(6)	5.2(5)	0.0(4)	3.8(4)
Cl62	33.3(5)	46.5(7)	22.5(5)	8.1(5)	7.1(4)	2.3(5)
O6	31.4(16)	31.1(16)	32.8(16)	-8.8(13)	12.6(13)	-3.3(13)

Table S4: Bond Lengths for $SeOCl_2$ in pm.

Atom	Atom	Length/pm	Atom	Atom	Length/pm
Se1	Cl11	216.7(1)	Se4	Cl41	217.9(1)
Se1	Cl12	217.77(1)	Se4	Cl42	218.2(1)
Se1	O1	167(3)	Se4	O4	161.4(3)
Se2	Cl21	217.4(1)	Se5	Cl51	218.8(1)
Se2	Cl22	217.34(1)	Se5	Cl52	220.0(1)
Se2	O2	161.2(3)	Se5	O5	161.0(3)
Se3	Cl31	216.5(1)	Se6	Cl61	217.9(1)
Se3	Cl32	217.9(1)	Se6	Cl62	219.9(1)
Se3	O3	161.6(3)	Se6	O6	159.6(3)

Table S5: Bond Angles for $SeOCl_2$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl11	Se1	Cl12	95.61(4)	Cl41	Se4	Cl42	96.43(5)
O1	Se1	Cl11	104.1(1)	O4	Se4	Cl41	103.5(1)
O1	Se1	Cl12	103.9(1)	O4	Se4	Cl42	103.3(1)
Cl22	Se2	Cl21	95.46(5)	Cl51	Se5	Cl52	94.54(4)
O2	Se2	Cl21	103.7(1)	O5	Se5	Cl51	102.3(1)
O2	Se2	Cl22	103.4(1)	O5	Se5	Cl52	102.6(1)
Cl31	Se3	Cl32	96.61(6)	Cl61	Se6	Cl62	95.94(5)
O3	Se3	Cl31	103.5(1)	O6	Se6	Cl61	103.8(1)
O3	Se3	Cl32	103.6(1)	O6	Se6	Cl62	103.2(1)
Cl11	Se1	Cl12	95.61(4)	Cl41	Se4	Cl42	96.43(5)
O1	Se1	Cl11	104.1(1)	O4	Se4	Cl41	103.5(1)

$[SeCl_3]_2[S_2O_7]$ (1)

Table S6: Crystallographic data of $[SeCl_3]_2[S_2O_7]$.

Empirical formula	$Cl_6O_7S_2Se_2$
Formula weight	546.762 g/mol
Temperature	100.00 K
Crystal system	monoclinic
Space group	$C2/c$ (No. 15)
Unit cell dimensions	a = 1200.88(4) pm b = 1830.82(7) pm c = 890.12(3) pm β = 132.218(1)°
Volume	1449.35(9) Å^3
Z	4
ρ_{calc}	2.506 g/cm^3
μ	6.507 mm^{-1}
F(000)	1037
Crystal size	0.33 × 0.09 × 0.07 mm^3
Radiation	MoK_α (λ = 0.71073 nm)
2Θ range for data collection	4.44 to 61.06
Index ranges	$-17 \leq h \leq 16$, $-26 \leq k \leq 25$, $-12 \leq l \leq 12$
Reflections collected	28440
Independent reflections	2212 [R_{int} = 0.0577, R_σ = 0.0219]
Completeness	99.6%
Absorption correction	multiscan
Min. and max. transmission	0.496 / 0.746
Data/restraints/parameters	2212/0/78
Goodness-of-fit on F^2	1.007
Final R indexes [$I \geq 2\sigma$ (I)]	R_1 = 0.0156, wR_2 = 0.0318
Final R indexes [all data]	R_1 = 0.0214, wR_2 = 0.0331
Largest diff. peak/hole	0.57/–0.69 e · Å^{-3}
CCDC-No.	2492705

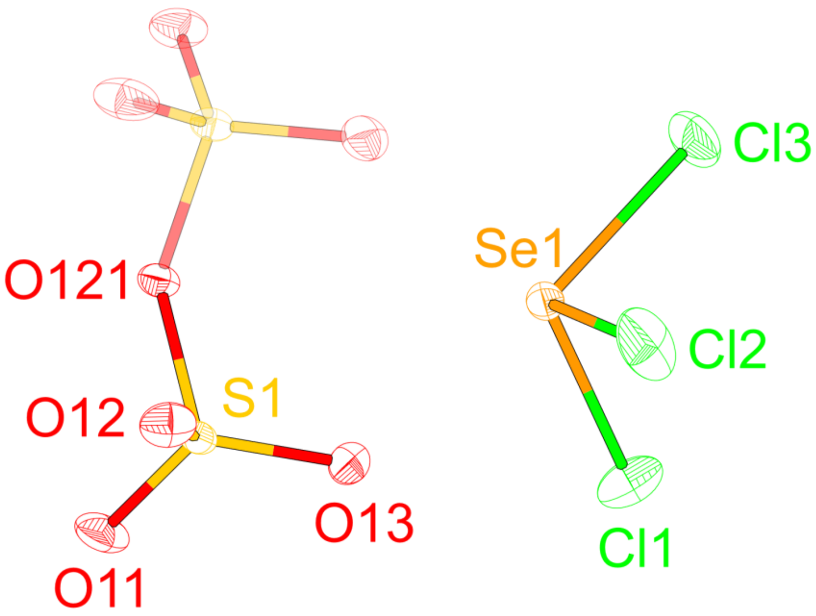

Figure S2: Thermal ellipsoid plot of the asymmetric unit of $[SeCl_3]_2[S_2O_7]$ shown with 50% probability. Atoms that are generated by symmetry operation for complete representation of the anion are shown at 50% visibility.

Table S7: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[SeCl_3]_2[S_2O_7]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Se1	7519.10(11)	3708.35(6)	7367.43(17)	15.24(4)
S1	3844.4(3)	3241.35(15)	2592.1(4)	12.87(6)
Cl3	9906.5(3)	3823.5(2)	9445.5(6)	31.96(9)
Cl2	7002.9(4)	4839.23(19)	7015.6(7)	39.82(10)
Cl1	7275.5(5)	3472.4(3)	9467.5(6)	42.54(10)
O121	5000	2822.1(6)	2500	13.8(2)
O12	3095.5(10)	3796.5(4)	1042.1(14)	20.72(19)
O11	2887.9(9)	2654.5(5)	2194.3(14)	21.72(19)
O13	4754.2(10)	3539.1(6)	4610.8(14)	26.0(2)

Table S8: Anisotropic Displacement Parameters ($Å^2\times10^3$) for $[SeCl_3]_2[S_2O_7]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Se1	11.82(6)	15.89(7)	17.12(6)	-0.15(4)	9.36(5)	-4.08(4)
S1	11.35(11)	12.63(13)	16.38(13)	-1.65(9)	10.03(11)	-2.18(10)
Cl3	12.43(12)	40.2(2)	30.58(17)	-2.08(13)	9.26(13)	-8.66(15)
Cl2	28.07(16)	16.66(17)	59.7(3)	-1.00(13)	23.32(17)	-13.71(16)
Cl1	49.3(2)	61.4(3)	39.1(2)	-8.0(2)	38.7(2)	-10.66(19)
O121	11.6(5)	14.5(5)	17.0(6)	0	10.3(5)	0
O12	22.8(4)	15.9(4)	28.2(5)	5.5(3)	19.1(4)	4.5(3)
O11	20.3(4)	16.9(4)	34.6(5)	-4.8(3)	21.2(4)	-1.8(4)
O13	16.8(4)	41.3(6)	21.2(5)	-4.9(4)	13.2(4)	-13.0(4)

Table S9: Bond Lengths for $[SeCl_3]_2[S_2O_7]$ in pm.

Atom	**Atom**	**Length/pm**	**Atom**	**Atom**	**Length/pm**
Se1	Cl3	213.50(3)	S1	O12	144.14(9)
Se1	Cl2	212.33(4)	S1	O11	143.27(8)
Se1	Cl1	212.17(4)	S1	O13	144.27(9)
S1	O121	163.54(6)			

Table S10: Bond Angles for $[SeCl_3]_2[S_2O_7]$.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
Cl2	Se1	Cl3	96.92(2)	O11	S1	O12	114.28(5)
Cl1	Se1	Cl3	99.01(2)	O13	S1	O121	106.37(4)
Cl1	Se1	Cl2	97.41(2)	O13	S1	O12	112.89(6)
O12	S1	O121	106.72(4)	O13	S1	O11	113.68(6)
O11	S1	O121	101.66(5)	S1[1]	O121	S1	124.02(7)

[1] 1-X, +Y, 1/2-Z

Table S11: Torsion Angles for $[SeCl_3]_2[S_2O_7]$.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
S1	O121	S1[1]	O12[1]	47.62(4)	O12	S1	O121	S1[1]	47.62(5)
S1	O121	S1[1]	O11[1]	167.64(4)	O11	S1	O121	S1[1]	167.64(4)
S1	O121	S1[1]	O13[1]	-73.15(5)	O13	S1	O121	S1[1]	-73.15(5)

[1] 1-X, +Y, 1/2-Z

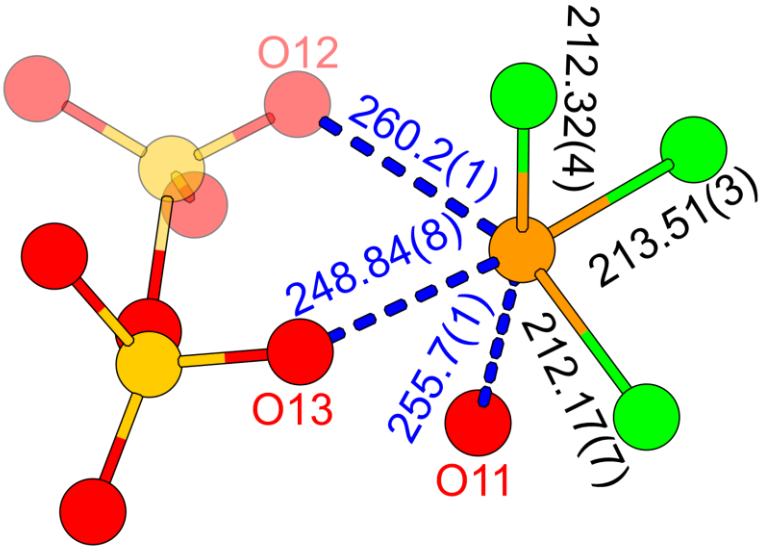

Figure S 3: Chalcogen-bonding within $[SeCl_3]_2[S_2O_7]$ and bond lengths of the opposite Se–Cl bonds. Distances are given in pm. Atoms that are generated by symmetry operation for complete representation of the anion are shown at 50% visibility.

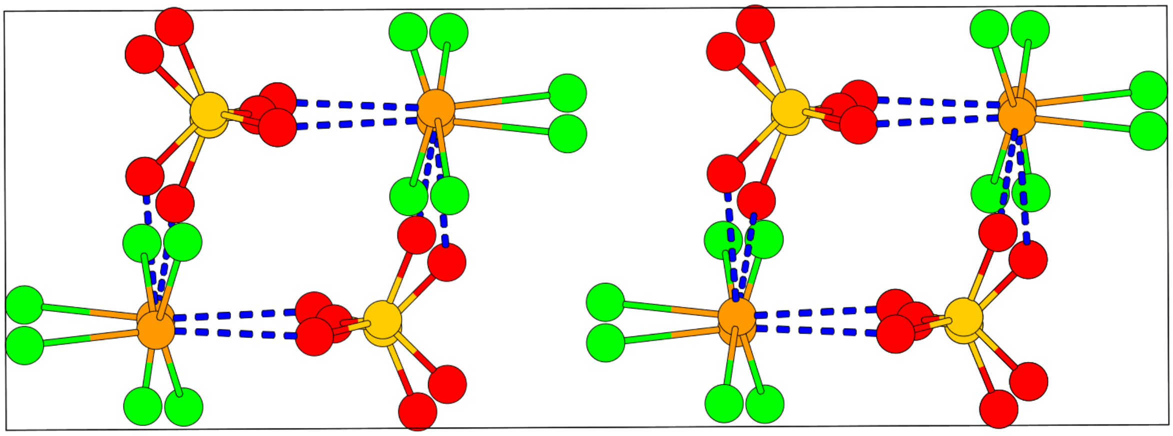

Figure S 4: Filled unit cell of $[SeCl_3]_2[S_2O_7]$, viewed along the crystallographic a-axis. Chalcogen-bonding within the units shown as dotted blue lines.

$[SeCl_3][ClSO_3]$ (2)

Table S12: Crystallographic data of $[SeCl_3][ClSO_3]$.

Empirical formula	Cl_4O_3SSe
Formula weight	300.82 g/mol
Temperature	100.00 K
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	a = 919.60(4) pm
	b = 958.99(3) pm
	c = 1879.26(2) pm
	α = 97.718(2)°
	β = 100.660(2)°
	γ = 97.718(2)°
Volume	1566.32(11) $Å^3$
Z	8
ρ_{calc}	2.551 g/cm^3
μ	6.360 mm^{-1}
F(000)	1136
Crystal size	0.21 × 0.03 × 0.02 mm^3
Radiation	MoK_α (λ = 0.71073 nm)
2Θ range for data collection	4.454 to 57.398
Index ranges	$-12 \leq h \leq 12$, $-11 \leq k \leq 12$, $-25 \leq l \leq 25$
Reflections collected	36329
Independent reflections	8070 [R_{int} = 0.0537, R_σ = 0.0489]
Completeness	99.9%
Absorption correction	multiscan
Min. and max. transmission	0.449 / 0.746
Data/restraints/parameters	8070/0/325
Goodness-of-fit on F^2	1.060
Final R indexes [$I \geq 2\sigma$ (I)]	R_1 = 0.0404, wR_2 = 0.874
Final R indexes [all data]	R_1 = 0.0541, wR_2 = 0.935
Largest diff. peak/hole	0.94/-0.89 e · $Å^{-3}$
CCDC-No.	2499372

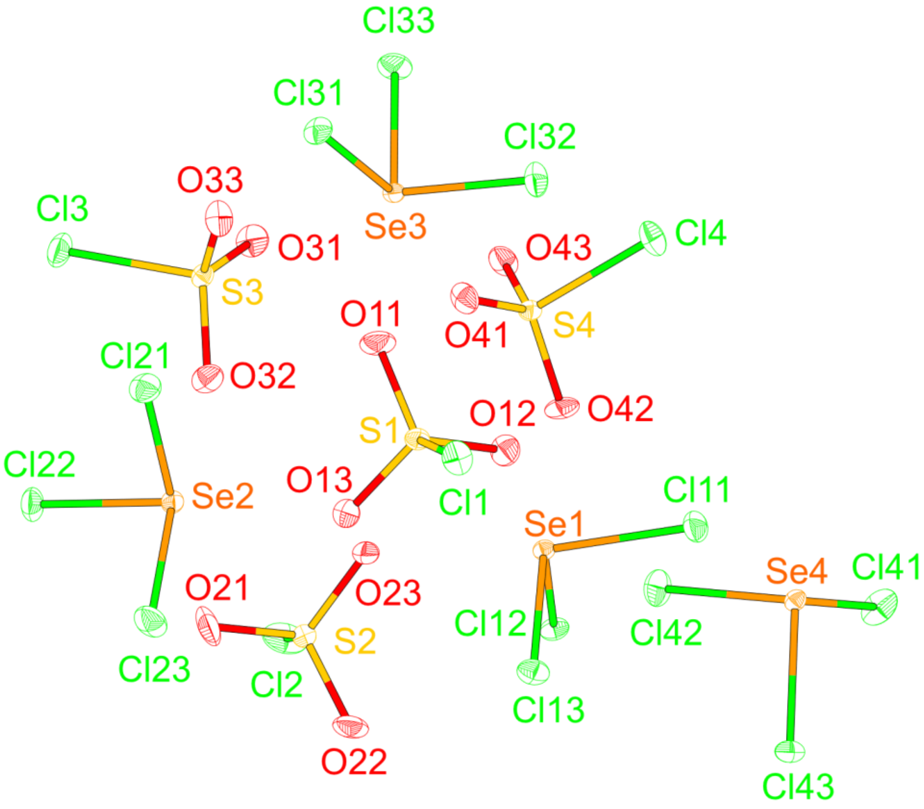

Figure S5: Thermal ellipsoid plot of the asymmetric unit $[SeCl_3][ClSO_3]$ shown with 50% probability.

Table S13: Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for $[SeCl_3][ClSO_3]$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Se1	1582.9(5)	1109.9(4)	3775.3(2)	8.74(9)
Cl11	3797.3(12)	1602.4(12)	4435.6(6)	17.3(2)
Cl12	369.5(12)	1509.6(11)	4647.6(6)	12.4(2)
Cl13	1792.3(13)	3201.1(11)	3507.2(6)	15.9(2)
Se2	-2080.0(5)	-578.0(5)	1077.8(2)	11.14(10)
Cl21	-1222.5(14)	-1690.6(13)	196.6(6)	18.9(2)
Cl22	-4413.5(12)	-1519.9(13)	641.0(6)	18.5(2)
Cl23	-1988.3(14)	1439.7(13)	736.1(7)	22.1(2)
Se3	1798.3(5)	-3746.1(4)	1649.6(2)	8.82(9)
Cl31	2002.0(13)	-4281.3(12)	522.4(6)	14.6(2)
Cl32	4136.9(12)	-2978.1(13)	2114.8(6)	18.1(2)
Cl33	1507.3(14)	-5915.6(12)	1835.0(7)	19.7(2)
Se4	7602.1(5)	4862.2(4)	3450.5(2)	9.31(9)
Cl41	7603.4(15)	4637.1(13)	4561.5(6)	21.7(3)
Cl42	5322.1(13)	3716.5(13)	3011.4(7)	22.6(2)

Cl43	7261.6(13)	7027.8(12)	3586.8(6)	17.0(2)
Cl1	3668.8(13)	1384.3(13)	1361.7(6)	18.3(2)
S1	2060.8(12)	189.1(11)	1806.6(6)	11.6(2)
O11	1871(4)	-1281(3)	1394.8(19)	21.0(7)
O12	2724(4)	455(4)	2568.9(17)	18.3(7)
O13	755(4)	776(4)	1660.7(18)	17.9(7)
Cl2	-3659.3(15)	73.4(14)	3525.1(8)	26.3(3)
S2	-2201.4(12)	916.8(12)	2898.6(6)	12.5(2)
O21	-3098(4)	554(5)	2171.8(19)	27.7(9)
O22	-1746(4)	2456(3)	3236(2)	21.8(8)
O23	-978(4)	179(3)	2969.5(18)	15.6(7)
Cl3	-4185.7(13)	-5461.0(13)	858.5(6)	20.2(2)
S3	-2186.3(12)	-4310.4(11)	1534.9(6)	10.3(2)
O31	-2114(4)	-5007(4)	2150.8(17)	19.0(7)
O32	-2346(4)	-2824(3)	1702.0(18)	18.0(7)
O33	-1075(4)	-4540(4)	1079.4(17)	16.8(7)
Cl4	3550.9(12)	-2903.9(13)	4014.1(6)	19.1(2)
S4	1374.6(12)	-2721.9(11)	3711.7(6)	9.7(2)
O41	1226(4)	-2753(4)	2938.0(17)	17.5(7)
O42	1333(4)	-1347(3)	4161.1(17)	16.1(7)
O43	477(4)	-3979(3)	3902.0(19)	17.9(7)

Table S14: Anisotropic Displacement Parameters (Å^2×10^3) for [$SeCl_3$][$ClSO_3$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Se1	10.2(2)	7.62(19)	8.5(2)	2.12(15)	2.21(15)	1.93(16)
Cl11	11.4(5)	19.3(5)	19.9(6)	4.0(4)	-0.3(4)	2.9(4)
Cl12	15.9(5)	11.2(5)	11.3(5)	1.6(4)	6.2(4)	3.8(4)
Cl13	18.3(5)	11.1(5)	20.8(6)	7.9(4)	6.0(4)	3.6(4)
Se2	11.8(2)	9.2(2)	11.7(2)	2.36(16)	0.21(16)	2.00(16)
Cl21	23.0(6)	19.5(6)	14.5(5)	1.8(4)	4.6(4)	6.9(5)
Cl22	12.1(5)	20.1(6)	19.3(6)	3.6(4)	-3.0(4)	0.0(4)
Cl23	20.1(6)	16.4(5)	31.6(7)	12.0(5)	1.0(5)	4.7(5)

Se3	11.4(2)	8.16(19)	7.48(19)	1.94(15)	1.90(15)	3.32(16)
Cl31	19.2(5)	16.4(5)	8.2(5)	0.7(4)	4.4(4)	5.0(4)
Cl32	11.6(5)	25.0(6)	15.8(5)	3.3(4)	-0.2(4)	2.9(4)
Cl33	27.4(6)	11.9(5)	22.4(6)	9.2(4)	3.1(5)	6.5(5)
Se4	10.4(2)	8.02(19)	8.9(2)	1.78(15)	1.67(16)	1.07(16)
Cl41	33.5(7)	19.0(6)	10.9(5)	4.9(4)	6.5(5)	0.0(5)
Cl42	11.0(5)	22.6(6)	29.1(6)	3.3(5)	-0.4(5)	-2.5(5)
Cl43	20.3(6)	13.0(5)	18.3(5)	0.8(4)	2.1(4)	8.2(4)
Cl1	16.2(5)	21.2(6)	18.9(6)	8.9(4)	4.9(4)	2.2(4)
S1	13.4(5)	8.8(5)	13.0(5)	3.7(4)	2.1(4)	2.9(4)
O11	31(2)	9.0(15)	23.9(18)	5.7(14)	2.8(15)	6.4(14)
O12	20.8(18)	22.9(18)	11.5(16)	2.0(13)	3.3(13)	7.0(14)
O13	15.0(16)	15.4(16)	21.0(17)	1.8(13)	0.0(13)	2.8(13)
Cl2	23.5(6)	22.5(6)	40.6(8)	12.6(5)	17.9(6)	9.7(5)
S2	12.6(5)	10.8(5)	13.1(5)	1.1(4)	0.4(4)	3.3(4)
O21	20.1(19)	47(2)	16.6(18)	1.2(16)	-4.4(15)	20.0(18)
O22	17.8(17)	9.0(15)	39(2)	6.1(14)	4.5(15)	4.7(13)
O23	13.6(16)	12.6(15)	19.3(17)	-1.0(13)	1.2(13)	5.1(13)
Cl3	13.6(5)	21.5(6)	19.1(6)	-2.8(4)	-1.3(4)	-0.7(4)
S3	12.0(5)	10.1(5)	8.0(5)	1.9(4)	1.4(4)	1.3(4)
O31	27.4(19)	21.2(18)	9.9(16)	5.7(13)	4.5(14)	6.9(15)
O32	25.8(19)	13.5(16)	14.5(16)	4.5(13)	2.5(14)	3.6(14)
O33	13.1(16)	25.6(18)	12.3(16)	6.2(13)	4.8(13)	2.4(14)
Cl4	11.3(5)	25.6(6)	22.0(6)	9.1(5)	1.8(4)	5.5(5)
S4	10.5(5)	8.1(5)	10.9(5)	2.4(4)	2.4(4)	2.4(4)
O41	20.2(17)	24.2(18)	10.6(15)	5.2(13)	2.3(13)	9.8(14)
O42	26.4(18)	6.4(14)	16.9(16)	4.6(12)	6.2(14)	3.7(13)
O43	13.9(16)	13.9(16)	26.8(18)	10.0(14)	1.3(14)	1.8(13)

Table S15: Bond Lengths for [$SeCl_3$][$ClSO_3$].

Atom	**Atom**	**Length/pm**	**Atom**	**Atom**	**Length/pm**
Se1	Cl11	214.7(1)	S1	O12	143.3(3)
Se1	Cl12	212.6(1)	S1	O13	144.5(3)

Se1	Cl13	213.3(1)	Cl2	S2	203.9(2)
Se2	Cl21	213.4(1)	S2	O21	143.8(4)
Se2	Cl22	212.9(1)	S2	O22	144.2(3)
Se2	Cl23	213.7(1)	S2	O23	145.3(3)
Se3	Cl31	212.9(1)	Cl3	S3	205.3(2)
Se3	Cl32	212.7(1)	S3	O31	144.0(3)
Se3	Cl33	214.0(1)	S3	O32	144.5(3)
Se4	Cl41	213.8(1)	S3	O33	144.4(3)
Se4	Cl42	212.5(2)	Cl4	S4	205.8(2)
Se4	Cl43	213.9(1)	S4	O41	143.6(3)
Cl1	S1	204.3(2)	S4	O42	143.9(3)
S1	O11	144.0(3)	S4	O43	144.4(3)

Table S16: Bond Angles for [SeCl$_3$][ClSO$_3$].

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
Cl12	Se1	Cl11	97.60(5)	O21	S2	Cl2	103.9(2)
Cl12	Se1	Cl13	96.44(4)	O21	S2	O22	115.0(2)
Cl13	Se1	Cl11	95.93(5)	O21	S2	O23	114.1(2)
Cl21	Se2	Cl23	98.61(5)	O22	S2	Cl2	103.8(2)
Cl22	Se2	Cl21	96.69(5)	O22	S2	O23	113.4(2)
Cl22	Se2	Cl23	96.34(5)	O23	S2	Cl2	105.0(2)
Cl31	Se3	Cl33	96.74(5)	O31	S3	Cl3	104.1(2)
Cl32	Se3	Cl31	98.42(5)	O31	S3	O32	115.2(2)
Cl32	Se3	Cl33	97.61(5)	O31	S3	O33	113.8(2)
Cl41	Se4	Cl43	97.95(5)	O32	S3	Cl3	104.3(2)
Cl42	Se4	Cl41	97.63(5)	O33	S3	Cl3	102.9(2)
Cl42	Se4	Cl43	97.44(5)	O33	S3	O32	114.6(2)
O11	S1	Cl1	103.1(2)	O41	S4	Cl4	104.3(1)
O11	S1	O13	113.5(2)	O41	S4	O42	114.5(2)
O12	S1	Cl1	104.0(2)	O41	S4	O43	115.4(2)
O12	S1	O11	115.2(2)	O42	S4	Cl4	104.0(2)
O12	S1	O13	114.9(2)	O42	S4	O43	113.9(2)

$[Se_2I_4]_2[S_4O_{13}]_2\cdot(SO_3)$ (3)

Table S17: Crystallographic data of $[Se_2I_4]_2[S_4O_{13}]_2\cdot(SO_3)$.

Empirical formula	$I_8O_{29}S_9Se_4$
Formula weight	2083.58 g/mol
Temperature	100.00 K
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	a = 993.8(1) pm b = 1013.7(1) pm c = 1045.9(2) pm α = 102.280(5)° β = 97.127(5)° γ = 94.689(2)°
Volume	1015.2(2) $Å^3$
Z	1
ρ_{calc}	3.408 g/cm^3
μ	10.245 mm^{-1}
F(000)	936
Crystal size	0.08 × 0.07 × 0.01 mm^3
Radiation	MoK_α (λ = 0.71073 nm)
2Θ range for data collection	4.028 to 57.424
Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$
Reflections collected	35166
Independent reflections	5257 [R_{int} = 0.0411, R_σ = 0.0263]
Completeness	99.7%
Absorption correction	Multiscan
Min. and max. transmission	0.486 / 0.746
Data/restraints/parameters	5257/0/244
Goodness-of-fit on F^2	1.114
Final R indexes [$I \geq 2\sigma$ (I)]	R_1 = 0.0387, wR_2 = 0.0790
Final R indexes [all data]	R_1 = 0.0465, wR_2 = 0.0829
Largest diff. peak/hole	1.53/–1.20 e · $Å^{-3}$
CCDC-No.	2492707

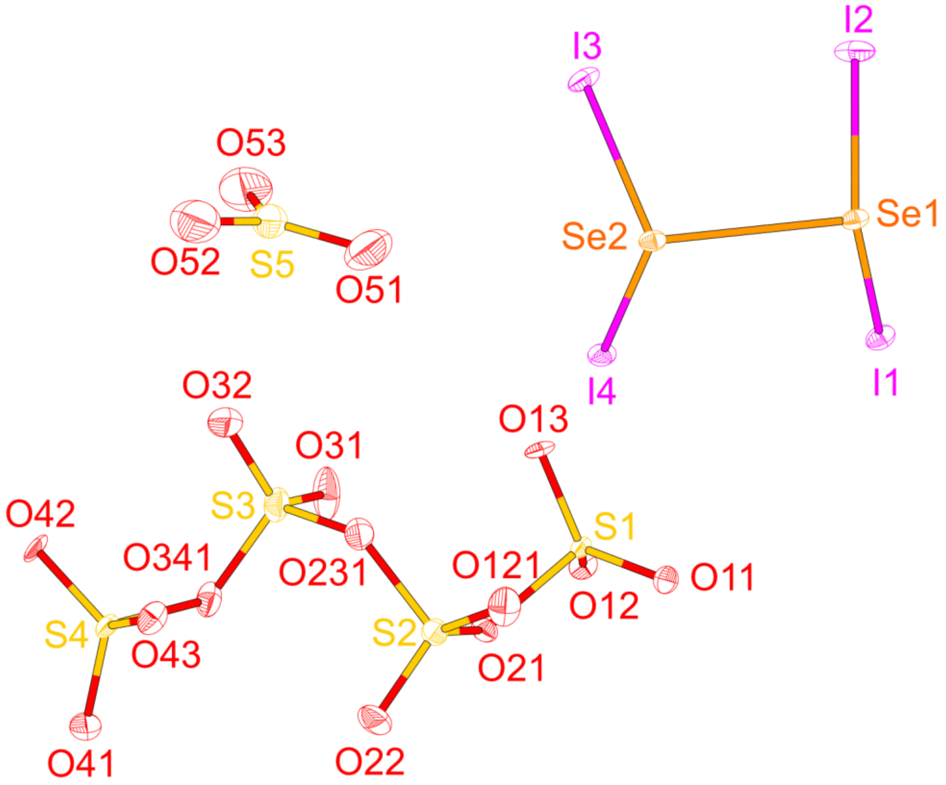

Figure S6: Thermal ellipsoid plot of the asymmetric unit $[Se_2I_4]_2[S_4O_{13}]_2{\cdot}(SO_3)$ shown with 50% probability.

Table S18: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for $[Se_2I_4]_2[S_4O_{13}]_2{\cdot}(SO_3)$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
I1	4597.0(4)	6755.1(4)	11363.4(4)	12.69(9)
I2	1959.3(5)	9377.4(5)	11561.1(5)	19.20(11)
I3	2103.7(4)	9593.0(4)	8136.5(5)	14.79(10)
I4	4827.8(4)	7209.6(4)	7966.0(4)	13.4(1)
Se1	2180.0(6)	6972.9(6)	10573.4(7)	10.56(13)
Se2	2339.4(6)	7162.6(6)	8041.2(6)	10.12(13)
S1	8460.4(15)	6771.9(15)	8331.3(15)	8.0(3)
S2	7750.4(17)	5297.4(16)	5615.8(16)	13.5(3)
S3	8138(2)	7814.6(18)	4721.6(17)	18.9(3)
S4	8453.3(16)	6523.8(15)	2012.4(16)	10.7(3)
O11	7862(5)	5703(5)	8843(5)	13.4(9)
O12	9802(5)	7392(5)	8933(5)	12.7(9)
O13	7534(4)	7716(4)	7986(5)	11.3(9)

O21	6562(6)	4744(5)	6018(5)	22.0(11)
O22	8431(6)	4543(6)	4658(5)	23.0(11)
O31	9042(7)	8493(6)	5872(5)	29.4(14)
O32	7134(7)	8495(6)	4113(6)	28.4(13)
O41	9573(5)	5797(5)	1672(5)	20.4(11)
O42	8328(6)	7765(5)	1589(5)	18.6(10)
O43	7183(5)	5697(5)	1961(5)	16.0(10)
O121	8856(5)	5977(5)	6812(5)	12.2(9)
O231	7218(5)	6583(5)	5060(5)	17.4(10)
O341	9015(5)	7103(5)	3726(5)	17.5(10)
S5	5326(4)	10244(4)	5041(5)	25.5(9)
O51	5040(30)	9420(20)	5910(30)	51(7)
O52	4690(30)	9960(20)	3800(20)	56(7)
O53	6264(18)	11410(14)	5445(16)	49(4)

Table S19: Anisotropic Displacement Parameters (Å^2×10^3) for $[Se_2I_4]_2[S_4O_{13}]_2\cdot(SO_3)$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
I1	9.57(18)	12.04(19)	16.9(2)	5.18(16)	-0.16(15)	1.79(14)
I2	19.2(2)	14.4(2)	20.3(2)	-3.54(17)	-3.23(17)	8.98(17)
I3	11.51(19)	11.05(19)	25.0(2)	9.95(17)	3.26(16)	3.08(14)
I4	9.62(18)	13.46(19)	20.2(2)	7.19(16)	6.18(15)	4.29(14)
Se1	7.8(3)	8.6(3)	15.8(3)	3.7(2)	1.7(2)	1.7(2)
Se2	7.0(3)	8.9(3)	14.7(3)	2.8(2)	1.7(2)	1.3(2)
S1	7.2(6)	7.8(6)	9.5(7)	3.7(5)	0.9(5)	0.7(5)
S2	16.9(7)	11.6(7)	11.2(7)	1.5(6)	1.1(6)	1.7(6)
S3	29.7(9)	16.0(8)	10.9(8)	3.7(6)	2.0(7)	1.4(7)
S4	11.8(7)	9.2(7)	12.8(7)	6.1(6)	1.8(6)	2.0(5)
O11	15(2)	12(2)	15(2)	5.4(18)	4.7(18)	0.8(17)
O12	10(2)	12(2)	15(2)	3.6(18)	-0.2(17)	-0.2(17)
O13	10(2)	7(2)	18(2)	4.3(17)	1.0(17)	4.5(16)
O21	29(3)	16(2)	18(3)	2(2)	1(2)	-5(2)
O22	32(3)	23(3)	13(2)	-2(2)	5(2)	11(2)

O31	48(4)	24(3)	11(3)	2(2)	0(2)	-16(3)
O32	45(4)	23(3)	22(3)	6(2)	10(3)	17(3)
O41	20(3)	24(3)	20(3)	8(2)	6(2)	11(2)
O42	36(3)	9(2)	15(2)	9.0(19)	5(2)	8(2)
O43	12(2)	15(2)	21(3)	8(2)	0.1(19)	-2.7(18)
O121	11(2)	14(2)	12(2)	1.8(18)	3.4(17)	3.1(17)
O231	17(2)	20(2)	16(2)	5(2)	3.0(19)	2.4(19)
O341	15(2)	24(3)	15(2)	10(2)	0.9(19)	1.7(19)
S5	31(3)	27(3)	18.8(18)	4.5(19)	2(2)	10.3(18)
O51	53(12)	46(12)	76(19)	41(13)	33(13)	26(11)
O52	70(16)	69(16)	30(9)	9(12)	2(9)	42(15)
O53	73(11)	23(7)	51(9)	1(6)	18(8)	7(7)

Table S20: Bond Lengths for $[Se_2I_4]_2[S_4O_{13}]_2\cdot(SO_3)$.

Atom	Atom	Length/pm	Atom	Atom	Length/pm
I1	Se1	248.46(8)	S2	O231	163.6(5)
I2	Se1	247.56(8)	S3	O31	141.6(6)
I3	Se2	247.59(8)	S3	O32	142.0(6)
I4	Se2	248.09(8)	S3	O231	161.2(5)
Se1	Se2	271.9(1)	S3	O341	154.0(5)
S1	O11	142.6(5)	S4	O41	142.4(5)
S1	O12	143.3(5)	S4	O42	143.0(5)
S1	O13	145.0(4)	S4	O43	144.6(5)
S1	O121	173.0(5)	S4	O341	176.7(5)
S2	O21	141.5(6)	S5	O51	140(2)
S2	O22	140.5(5)	S5	O52	133(3)
S2	O121	155.4(5)	S5	O53	139.8(2)

Table S21: Bond Angles for $[Se_2I_4]_2[S_4O_{13}]_2\cdot(SO_3)$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
I1	Se1	Se2	100.84(3)	O31	S3	O32	121.3(4)
I2	Se1	I1	102.76(3)	O31	S3	O231	109.0(3)
I2	Se1	Se2	99.34(3)	O31	S3	O341	107.0(4)

I3	Se2	I4	98.99(3)	O32	S3	O231	101.9(3)
I3	Se2	Se1	102.43(3)	O32	S3	O341	111.9(3)
I4	Se2	Se1	102.10(3)	O341	S3	O231	104.2(3)
O11	S1	O12	117.9(3)	O41	S4	O42	117.8(3)
O11	S1	O13	115.0(3)	O41	S4	O43	115.6(3)
O11	S1	O121	104.9(3)	O41	S4	O341	98.4(3)
O12	S1	O13	114.4(3)	O42	S4	O43	115.4(3)
O12	S1	O121	98.4(3)	O42	S4	O341	102.4(3)
O13	S1	O121	102.7(3)	O43	S4	O341	103.2(3)
O21	S2	O121	112.1(3)	S2	O121	S1	122.9(3)
O21	S2	O231	102.3(3)	S3	O231	S2	127.4(3)
O22	S2	O21	122.5(3)	S3	O341	S4	124.2(3)
O22	S2	O121	106.6(3)	O51	S5	O53	121.3(1)
O22	S2	O231	108.1(3)	O52	S5	O51	121.4(1)
O121	S2	O231	103.6(3)	O52	S5	O53	117.3(1)

Table S22: Torsion Angles for $[Se_2I_4]_2[S_4O_{13}]_2\cdot(SO_3)$.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O11	S1	O121	S2	67.8(4)	O32	S3	O231	S2	172.0(4)
O12	S1	O121	S2	-170.3(3)	O32	S3	O341	S4	-26.7(5)
O13	S1	O121	S2	-52.8(4)	O41	S4	O341	S3	-171.3(4)
O21	S2	O121	S1	-32.2(4)	O42	S4	O341	S3	67.7(4)
O21	S2	O231	S3	166.8(4)	O43	S4	O341	S3	-52.5(4)
O22	S2	O121	S1	-168.8(3)	O121	S2	O231	S3	50.1(4)
O22	S2	O231	S3	-62.7(5)	O231	S2	O121	S1	77.3(4)
O31	S3	O231	S2	-58.5(5)	O231	S3	O341	S4	82.7(4)
O31	S3	O341	S4	-161.9(4)	O341	S3	O231	S2	55.4(5)

Table S23: Atomic Occupancy for $[Se_2I_4]_2[S_4O_{13}]_2\cdot(SO_3)$.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
S5	0.5	O52	0.5	O51	0.5
O53	0.5				

Table S 24: S–O bond lengths (in pm) and δ-values (terminal SO_3) groups of literature-known tetrasulfate compounds. [TS] = $[S_4O_{13}]^{2-}$.

Bond	$[Se_2I_4]_2$ $[TS]_2\cdot(SO_3)$	$[Te_6]$ $[TS]_2$[10]	$[I_3]_4$ $[TS]_2(SO_3)$[11]	Ba [TS][b] [12]	$[NO_2]_2$ [TS][a] [13]	Li_2 [TS][11]
S1–O11	142.6(5)	142.4(5)	142.8(9)–144(1)	142.6(8)	142.0	143.1(2)
S1–O12	143.3(5)	142.8(5)	143(1)–144.3(9)	142.7(8)	142.3	142.5(2)
S1–O13	145.0(4)	143.2(5)	143(1)–145(1)	142.6(8)	142.3	142.4(2)
δ(S1)	*10.64*	*10.33*	*10.52*	*9.20*	*9.80*	*9.57*
S1–O121	173.0(5)	176.4(5)	171.2(9)–174.0(9)	178.7(8)	176.6	176.5(2)
S2–O21	141.5(6)	140.7(5)	140(1)–141.2(9)	141.9(8)	141.4	140.9(2)
S2–O22	140.5(5)	142.3(4)	141(1)–141(1)	142.0(8)	141.1	141.0(2)
S2–O121	155.4(5)	154.1(5)	155.6(9)–155.7(9)	152.4(8)	153.0	152.4(2)
S2–O231	163.6(5)	160.9(5)	162(1)–163.3(9)	161.8(5)	163.9	162.8(2)
S3–O31	141.6(6)	141.9(5)	141(1)–141.5(9)	141.9(8)	141.3	141.7(2)
S3–O32	142.0(6)	141.3(5)	140(1)–144(1)	142.0(8)	142.0	140.9(2)
S3–O231	161.2(5)	163.9(5)	161.3(9)–162.8(9)	161.8(5)	160.9	161.7(2)
S3–O341	154.0(5)	152.7(5)	155.5(9)–156.7(9)	152.4(8)	153.4	153.2(2)
S4–O41	142.4(5)	142.1(5)	142.4(9)–143.9(8)	142.6(8)	142.1	142.1(2)
S4–O42	143.0(5)	142.1(5)	142.9(9)–146(1)	142.7(8)	143.1	141.8(2)
S4–O43	144.6(5)	143.5(5)	142.4(9)–144.0(8)	142.6(8)	143.1	142.1(2)
δ(S4)	*9.99*	*9.87*	*10.50*	*9.20*	*9.52*	*9.85*
S4–O341	176.7(5)	175.6(5)	172.3(9)–174.7(8)	178.7(8)	177.0	175.3(2)

a – the average lengths were calculated, b – symmetry plane through the anion leads to S3 = S2 and S4 = S1.

C. Delta Values

The delta values (in the following written as δ) were calculated using the *Polynator* software package, as we have described before.[14] Therein, δ is calculated as follows:

$$\delta = 100\left(\frac{\sum_i |\boldsymbol{a_i} - \boldsymbol{v_i}|^2}{\sum_i |\boldsymbol{a_i} - \boldsymbol{c}|^2}\right)^{1/2} \tag{1.0}$$

where $\mathbf{a_i}$ is an atom vector, $\mathbf{v_i}$ is the vector the corresponding model vertex and **c** is the centroid of all atom vectors.[15]

The *.cif* files from the analyzed substances were taken from the ICSD/CCDC websites and used without further modification. Within the software, the central and ligand atoms were defined as sulfur and oxygen, respectively. The terminal SO_3 units could be identified in most cases by adjusting the distance connectivity criterium to a maximum value of 1.6 Å. For the analysis, the generated δ values for the geometric object 'triangle[regular] (–6m2, 1 °f' were taken. If 'tripod[3m] (2 °f)' would be chosen as the geometric object, the correction of the central atoms' distortion would lead to values not suitable for comparison.

D. Computational Details

To ensure the theoretical models accurately reflect the experimental data, the calculations were performed on molecular clusters derived directly from the X-ray diffraction crystal structures.

All density functional theory (DFT) calculations were performed using the TURBOMOLE 7.7 program package[16] and the X-ray coordinates. The PBE0 hybrid functional[17] with the D4 dispersion correction[18] was employed, in conjunction with the def2-TZVP basis set.[19] For iodine atoms, effective core potentials (ECPs) including scalar relativistic effects were utilized to account for relativistic contributions.[20]

To analyze the nature of noncovalent interactions, the quantum theory of atoms in molecules (QTAIM) analysis[21-22] was performed using the Multiwfn program.[23] The topological parameters, including bond critical points (BCPs) and electron density values, were extracted to characterize halogen and chalcogen bonding interactions. The chalcogen bond interaction energies were obtained through an energy descriptor ($E_{int} = 0.375\ V(r)$) based on the potential energy density (V) found in a bond Critical Point (bcp) interconnecting the chalcogen atom with the Lewis base.[24]

Natural Bond Orbital (NBO) analysis[25] was conducted using the NBO 7.0 program[26] to investigate orbital donor-acceptor interactions and quantify stabilization energies associated with LP(O)→σ* charge transfer. The second-order perturbation energies provided insights into the electronic contributions to halogen bonding interactions.

Additional Results and Discussion

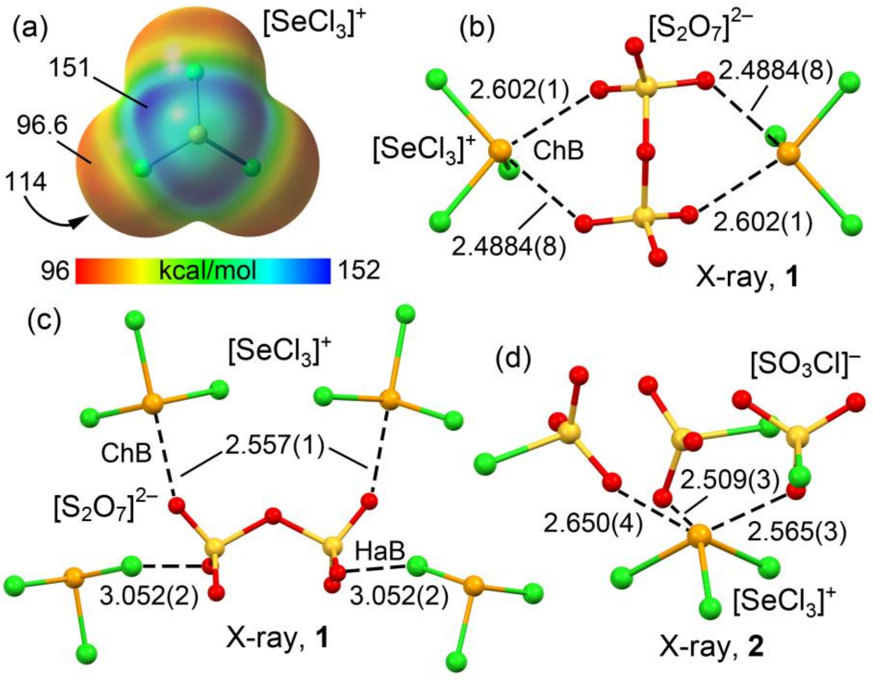

Figure S 7: (a) MEP surface of the $[SeCl_3]^+$ cation (isosurface 0.001 a.u.) with energies at selected points in kcal/mol. (b,c) Partial views of the X-ray structure of salt **1** showing the chalcogen bonding assemblies. (d) Partial view of the X-ray structure of salt **2**. Distances in [Å].

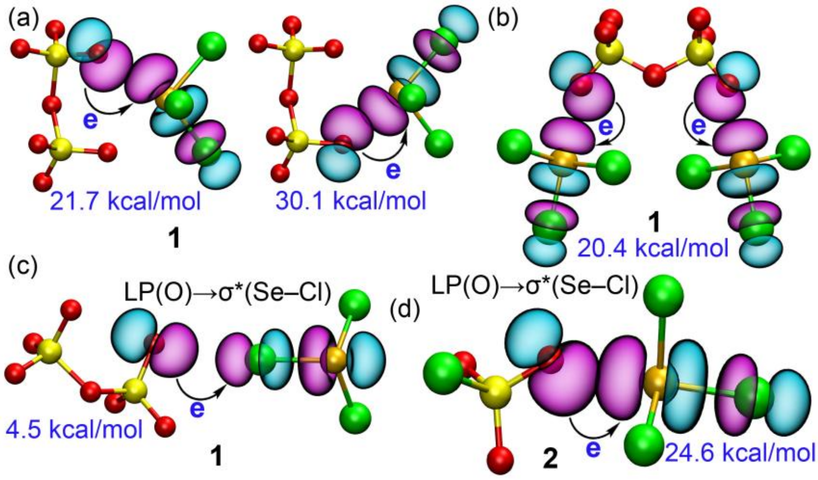

Figure S 8: NBO analysis of the chalcogen and halogen bonded dimers in compounds 1 and 2. The donor-acceptor interactions (LP→σ*) and the associated second-order perturbation energies $E^{(2)}$ in kcal/mol are indicated.

The magnitude of the perturbation energies is attributed to the short intermolecular distances, which facilitate strong orbital overlap. It is worth noting that while these $E^{(2)}$ values are significantly larger than the total interaction energies discussed previously, they are not directly comparable; the orbital stabilization is largely compensated by the steric exchange-repulsion term arising from the close proximity of the interacting units. In the case of the halogen bond, a similar LP(O)→σ* (Cl–Se) electron transfer mechanism is observed. However, due to the much longer Cl···O distance compared to the Se···O contacts, the orbital overlap is less effective, resulting in a more modest $E^{(2)}$ energy of 4.5 kcal/mol.

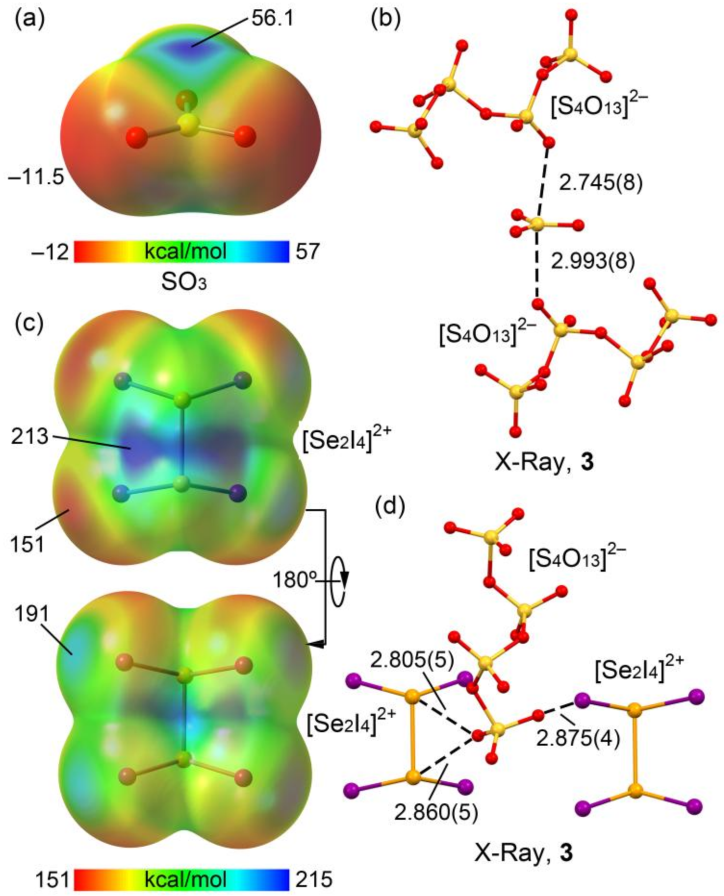

Figure S 9: (a) MEP surface of the SO_3 molecule (isosurface 0.001 a.u.) with energies at selected points in kcal/mol. (b) Partial view of the X-ray structure of 3 showing the π-hole interactions of the SO_3 molecule. (c) Two views of the MEP surface of the $[Se_2I_4]^{2+}$ dication (isosurface 0.001 a.u.) showing the merged σ-holes. (d) Partial view of the X-ray structure of 3 showing the competition between ChB and HaB interactions.

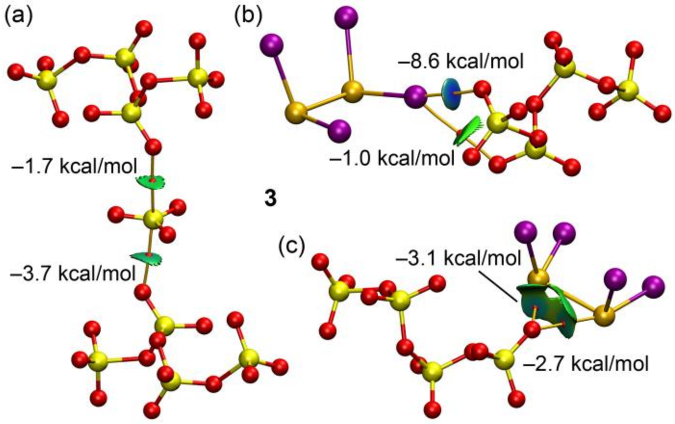

Figure S 10: QTAIM/NCIplot analysis of the non-covalent assemblies in compound **3**. (a) π-hole interactions involving SO_3 and two anions. (b) Halogen bonding interactions between $[Se_2I_4]^{2+}$ and the anion. (c) Bifurcated chalcogen bonding interactions between $[Se_2I_4]^{2+}$ and the anion. The interaction energies in kcal/mol are indicated.

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