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Chalcogen Bonding of Two Ligands to Hypervalent YF_4 (Y=S, Se, Te, Po)

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Table S1. Structural parameters (distances in Å, angles in degrees) for isolated monomers of YF_4 calculated at MP2/aug-cc-pVTZ level.

isolated monomer	r(Y-F_e)	r(Y-F_a)	∠(F_e-Y-F_e)	∠(F_a-Y-F_a)	Σ∠(F_e-Y-F_a)[a]
SF_4	1.607	1.704	101.4	172.3	350.4
SeF_4	1.723	1.804	100.5	169.2	346.0
TeF_4	1.881	1.945	100.9	163.2	338.8
PoF_4	1.972	2.049	99.2	168.2	344.8

[a] sum of four F_e-Y-F_a angles.

Table S2. Harmonic frequencies (cm^{-1}) and infrared intensities (km/mol)[a] calculated for isolated YF_4 monomers at MP2/aug-cc-pVDZ level of theory. Assignment is based on the calculated potential energy distribution (PED).

	SF_4	SeF_4	TeF_4	PoF_4	PED (%)[b]
1	856 (98.5)	738 (55.6)	684 (55.4)	642 (47.2)	ν_s(Y-F_e)
2	837 (173.4)	722 (111.5)	676 (100.1)	631 (90.9)	ν_a(Y-F_e)
3	758 (643.0)	642 (370.8)	610 (275.5)	550 (268.4)	ν_a(Y-F_a)
4	559 (2.7)	579 (1.5)	579 (0.1)	560 (0.6)	ν_s(Y-F_a)
5	476 (0.4)	382 (11.9)	305 (14.8)	245 (10.2)	wag(Y-F_e)
6	476 (20.5)	348 (27.2)	272 (33.0)	205 (25.4)	def (F-Y-F)
7	414 (0.0)	347 (0.0)	288 (0.0)	233 (0.0)	twist(Y-F_a)
8	315 (10.7)	234 (13.1)	181 (14.5)	120 (17.1)	wag(Y-F_a)
9	201 (1.1)	160 (1.1)	116 (0.9)	92 (4.6)	def(F-Y-F)

[a] IR intensity value shown in parentheses. [b] PED from the calculations for the SF_4 monomer. The predominant components of the PED matrix or their linear combination (e.g., stretching or bending). Abbreviations: ν_s, symmetric stretching; ν_a, antisymmetric stretching; wag, wagging deformation; def, out-of-plane deformation; twist, twisting deformation.

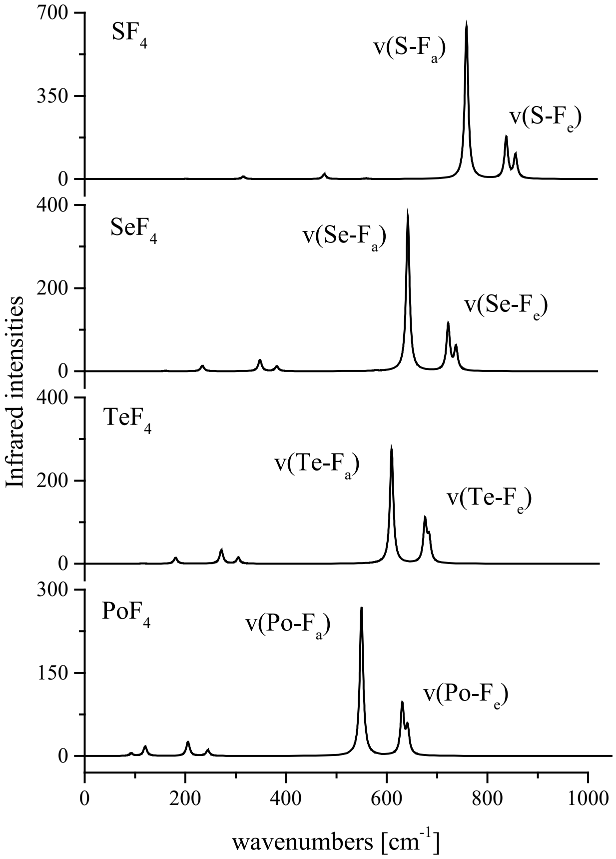
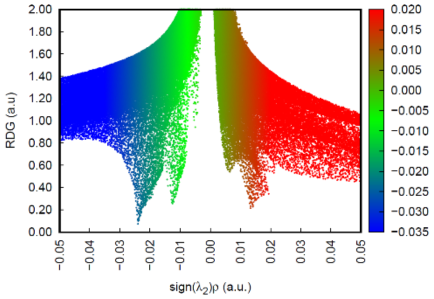
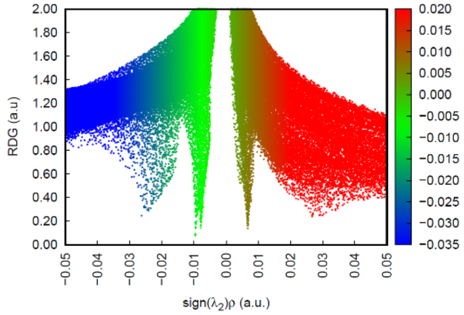
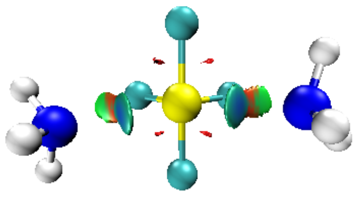
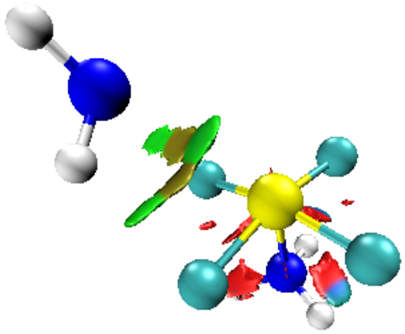
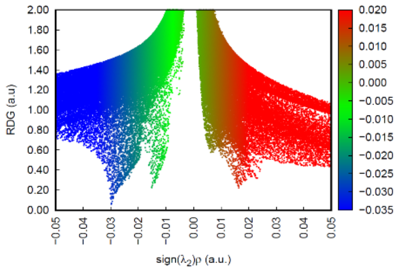
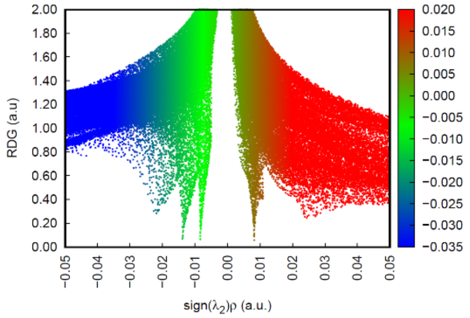
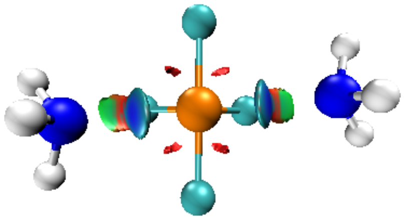
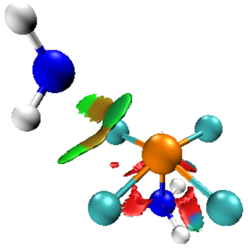
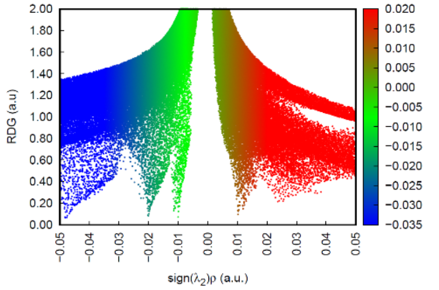
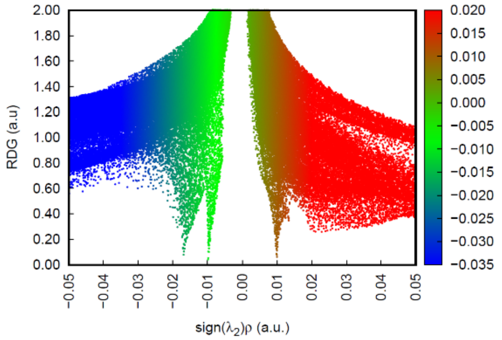
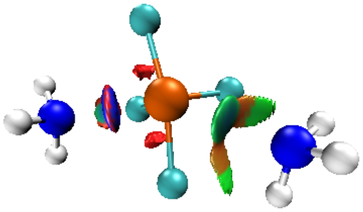
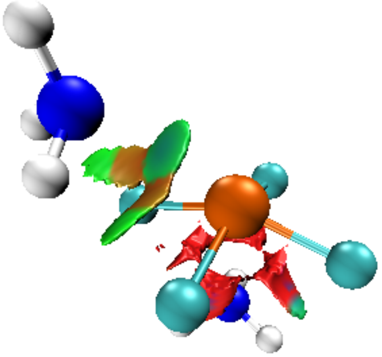
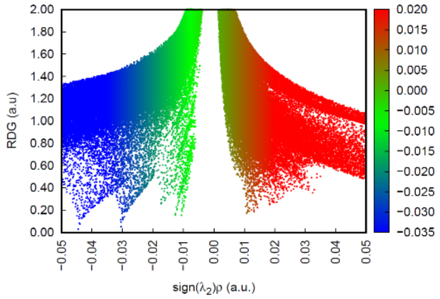
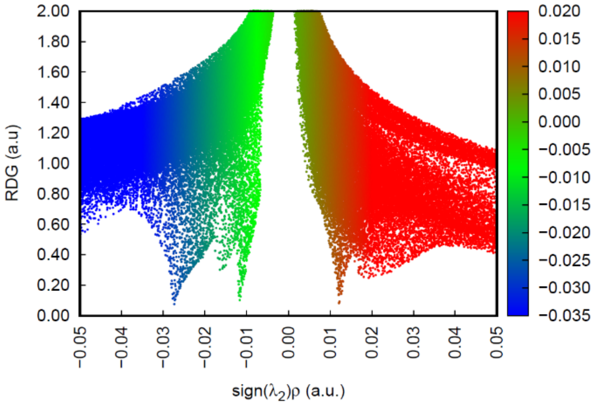
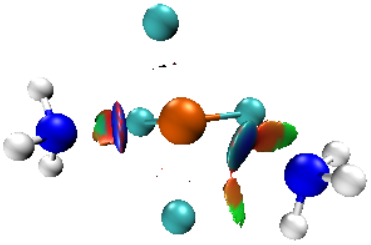
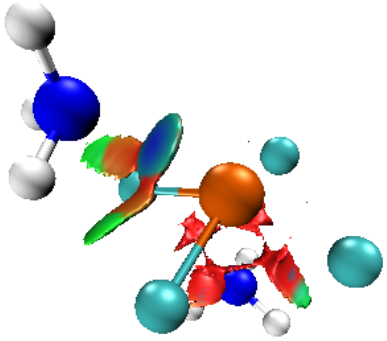


Fig. S1. Infrared spectra of isolated YF_4 calculated at MP2/aug-cc-pVDZ level.

Fig S2. NCI diagrams for *cis* and *trans* complexes. Colors represent: red – strong steric repulsions, brown – light repulsion, green – van der Waals interactions, blue – strong attraction.

	cis	*trans*
$(H_3N)_2\cdots SF_4$		
$(H_3N)_2\cdots SF_4$		
$(H_3N)_2\cdots SeF_4$		
$(H_3N)_2\cdots SeF_4$		

$(H_3N)_2\cdots TeF_4$		
$(H_3N)_2\cdots TeF_4$		
$(H_3N)_2\cdots PoF_4$		
$(H_3N)_2\cdots PoF_4$		

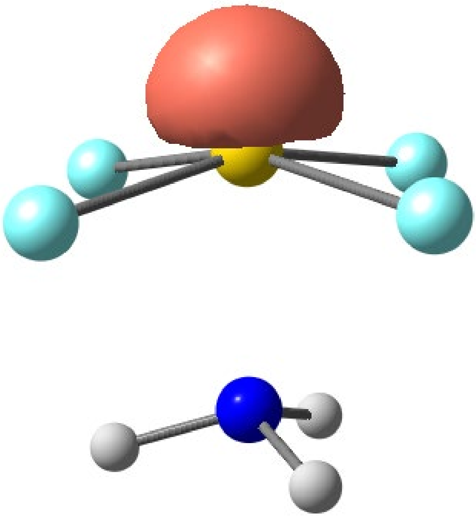


Fig. S3. Depiction of lone pair orbital of the S atom in the $(H_3N)\cdots SF_4$ complex (more distant NH_3 was removed) in full complex geometry of the trimer, on the 0.20 au isodensity surface.

Table S3. Deformation energies (E_{def}, kcal/mol) of YF_4 complexes with 2 NH_3 calculated at the MP2/ aug-cc-pVDZ level of theory.

	E_{def} of YF_4	E_{def} of LBs	sum	$V_{S,max}$	$V_{S,max}$
cis				N' removed	N removed
$(H_3N)_2\cdots SF_4$	1.87	0.01/0.01	1.89	29.5	29.4
$(H_3N)_2\cdots SeF_4$	2.93	0.03/0.03	2.99	35.3	35.5
$(H_3N)_2\cdots TeF_4$	6.03	0.64/0.15	6.82	42.5	44.7
$(H_3N)_2\cdots PoF_4$	4.64	0.70/0.11	5.45	55.2	54.6
trans					
$(H_3N)_2\cdots SF_4$	46.32	1.31/0.01	47.64	4.3	64.3
$(H_3N)_2\cdots SeF_4$	32.79	1.10/0.01	33.90	15.5	64.9
$(H_3N)_2\cdots TeF_4$	19.89	0.69/0.61	21.16	28.0	74.0
$(H_3N)_2\cdots PoF_4$	17.10	0.77/0.61	18.48	51.2	72.9

[c] MEP extrema values (designated on the 0.001 isosurface) of $(H_3N)\cdots SF_4$ in full complex geometry, N' means that the distant ligand was removed, while N means that closer ammonia ligand was removed.

Table S4. AIM descriptors (au) of *cis* and *trans* complexes. Bond critical point (BCP) properties: electron density ρ, Laplacian of electron density $\nabla^2\rho$, and total electron energy H, were obtained at the MP2/ aug-cc-pVDZ level.

	interaction	ρ	$\nabla^2\rho$	H
$(H_3N)_2\cdots SF_4$	S1 - N6	0.024	+0.072	+0.001
	S1 - N13	0.024	+0.073	+0.001
$(H_3N)_2\cdots SeF_4$	Se1 - N6	0.030	+0.075	-0.001
	Se1 - N13	0.030	+0.075	-0.001
$(H_3N)_2\cdots TeF_4$	N5 - Te15	0.048	+0.089	-0.008
	N12-Te15	0.020	+0.049	-0.0001
$(H_3N)_2\cdots PoF_4$	N5 - Po14	0.045	+0.112	-0.004
	N12- Po14	0.031	+0.078	-0.001
$(H_3N)_2\cdots SF_4$	S1 - N6	0.160	-0.301	-0.141
	S1 - N7	0.010	+0.033	+0.001
	F4 - H12	0.008	+0.038	+0.001
	F5 - H13	0.008	+0.038	+0.001
$(H_3N)_2\cdots SeF_4$	Se1 - N6	0.123	+0.038	-0.070
	Se1 - N7	0.014	+0.042	+0.001
	F4 - N7	0.008	+0.040	+0.001
	F5 - N7	0.008	+0.040	+0.001
$(H_3N)_2\cdots TeF_4$	N12- Te14	0.086	+0.191	-0.025
	N11- Te15	0.017	+0.044	+0.0003
$(H_3N)_2\cdots PoF_4$	N13- Po14	0.080	+0.218	-0.016
	N12- Po17	0.028	+0.072	-0.001

Table S5. Calculated frequencies (cm^{-1}) and infrared intensities (km/mol)[a] calculated for *cis* complexes at MP2/aug-cc-pVDZ level of theory. Assignment is based on the calculated potential energy distribution (PED).

	S	Se	Te	Po	Assignment [d]
1	811 (184.2)	688 (118.1)	638 (98.5)	588 (98.9)	νs(Y-F_e)
2	787 (281.5)	662 (181.9)	605 (150.9)	560 (137.7)	νa(Y-F_e)
3	701 (649.4)	584 (429.9)	567 (266.5)	479 (170.7)	νa(Y-F_a)
4	523 (1.4)	537 (1.5)	526 (5.0)	512 (18.3)	νs(Y-F_a)
5	464 (27.5)	343 (78.1)	298 (47.4)	236 (35.3)	def (F-Y-F)
6	141 (3.9)	155 (8.3)	251 (66.1)	262 (33.4)	νs(Y···N)[c]
7	104 (4.4)	80 (5.0, 1.5)	139 (22.3)	203 (56.5)	νa(Y···N')[d]

[a] IR intensity value are shown in brackets. [b] Assignment from PED calculations. The predominant components of the PED matrix or their linear combination (e.g., stretching or bending). [c] ν(Y···N) for Y= Te, Po. [d] ν(Y···N') for Y= Te, Po.
Abbreviations: ν_s, symmetric stretching; ν_a, antisymmetric stretching; def, out-f-plane deformation.

Table S6. Calculated frequencies (cm^{-1}) and infrared intensities (km/mol)[a] calculated for *trans* complexes at MP2/aug-cc-pVDZ level of theory. Assignment is based on the calculated potential energy distribution (PED).

	S	Se	Te	Po	Assignment [b]
1	679 (80.3)	598 (26.0)	572 (29.2)	542 (21.2)	νs(Y-F)
2	632 (450.3)	562 (326.1)	547 (259.1)	506 (244.6)	νa(Y-F)
3	630 (465.1)	561 (336.0)	546 (273.9)	503 (251.6)	νs(Y-F)
4	471 (0.1)	497 (0.0)	508 (0.5)	494 (17.3)	νs(Y-F)
5	485 (65.1)	363 (58.5)	283 (149.8)	235 (110.5)	def(F-Y-F)
6	432 (5.5)	432 (3.4)	405 (1.0)	401 (43.1)	ν(Y…N)
7	116 (5.1)	130 (7.2)	135 (13.2)	187 (18.7)	ν(Y…N')

[a] IR intensity value are shown in brackets. [b] Assignment from PED calculations. The predominant components of the PED matrix or their linear combination (e.g., stretching or bending). Abbreviations: ν_s, symmetric stretching; ν_a, antisymmetric stretching; def, out-of-plane deformation.

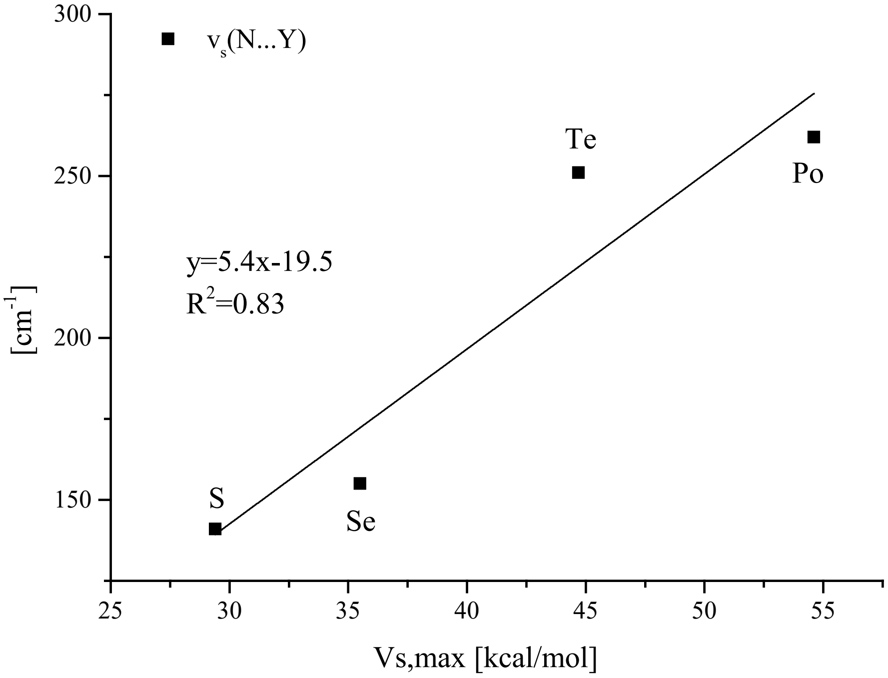


Fig S4. Linear correlation between v$_s$(Y··N) versus $V_{s,max}$ (closer NH_3 removed) in *cis* complexes $(H_3N)_2$···YF_4.