Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Stable and metastable crystal structures and ammonia dynamics in strontium chloride ammines

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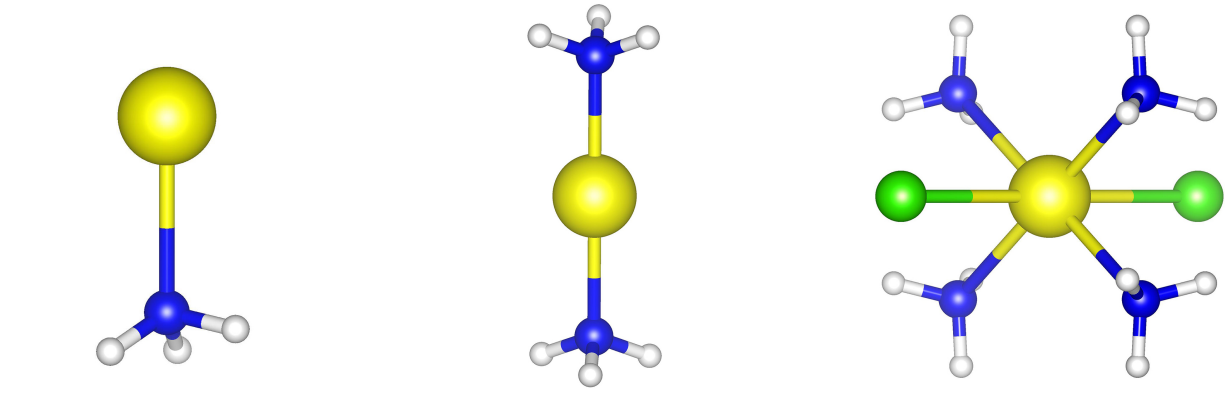
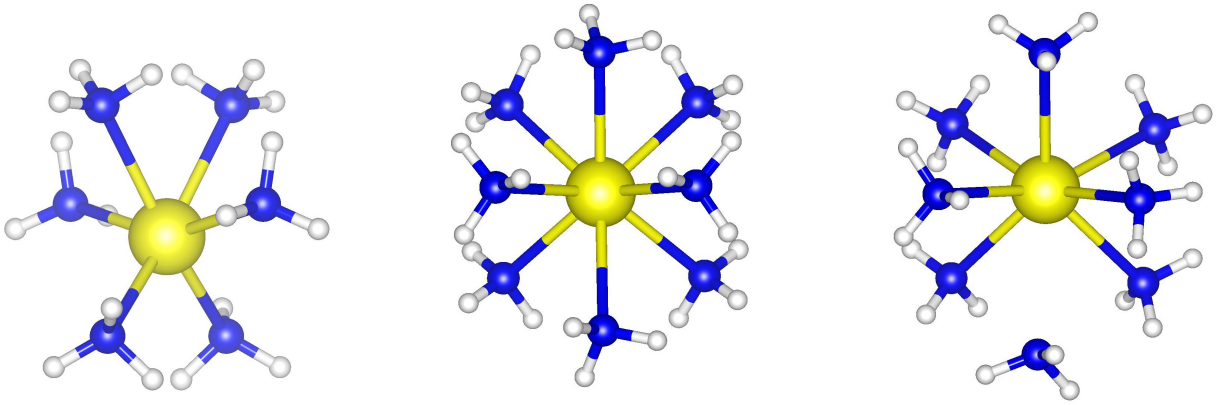
Table S1: Bond distance thresholds (in Å) used for the crystal structure prediction of each phase.

Bond Distance Threshold	**SrN1Cl2**	**SrN2Cl2**	**SrN4Cl2**	**SrN6Cl2**	**SrN8Cl2**
Cl − Cl	3.30	3.30	5.00	5.20	5.20
Cl − H				2.30	2.30
Cl − N	3.00	3.00	3.20		
H − H	1.50	1.50	1.50		
N − N	2.73	2.73	2.73		
Sr − Cl	2.90	2.90	4.50	4.80	4.80
Sr − H		2.70			
Sr − N	2.48	2.48	2.48		
Sr − Sr	4.20	4.20	7.00	7.00	7.00



$Sr(NH_3)$ $Sr(NH_3)_2$ $Sr(NH_3)_4Cl_2$



$Sr(NH_3)_6$ $Sr(NH_3)_8$ $Sr(NH_3)_7 + NH_3$

Figure S1: Different Sr coordinations used in the crystal structure prediction of each phase.

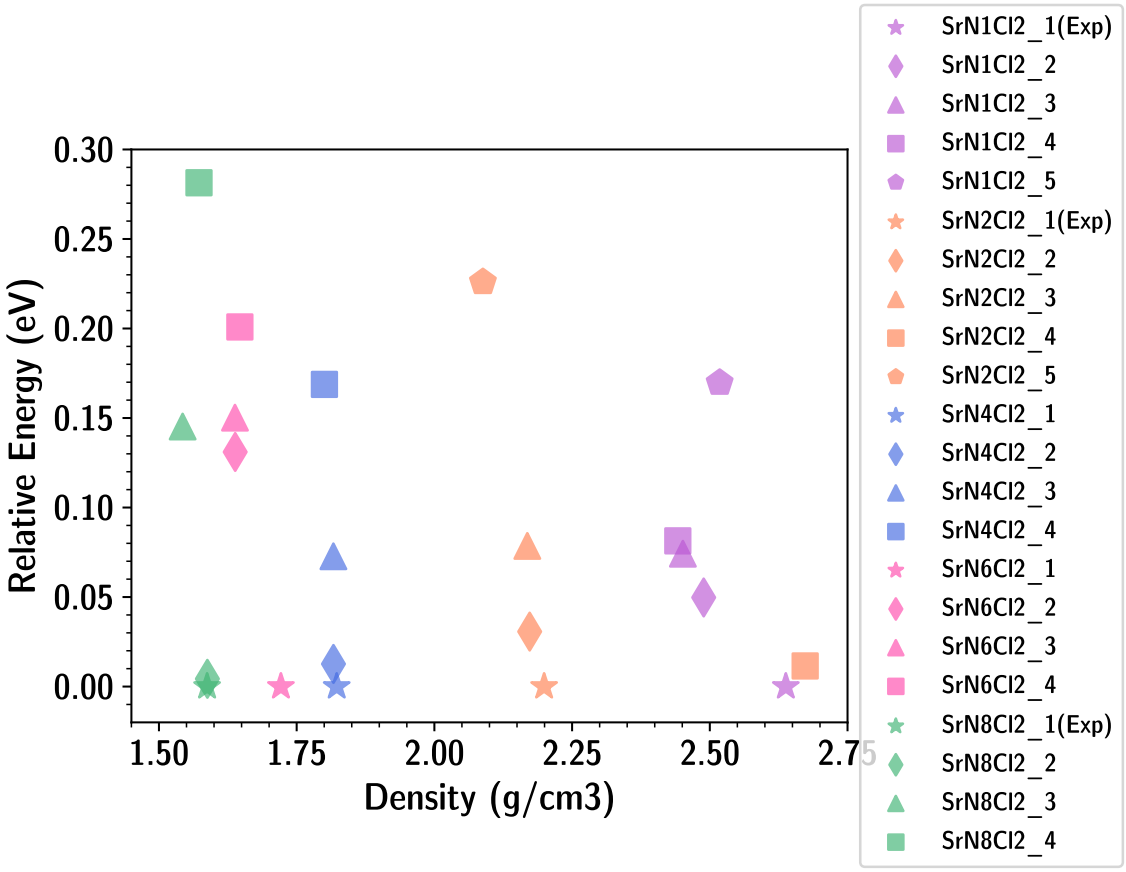


Figure S2: Relative energy-density relationships at PBEsol-D3 level of calculations for all considered predicted crystal structures.

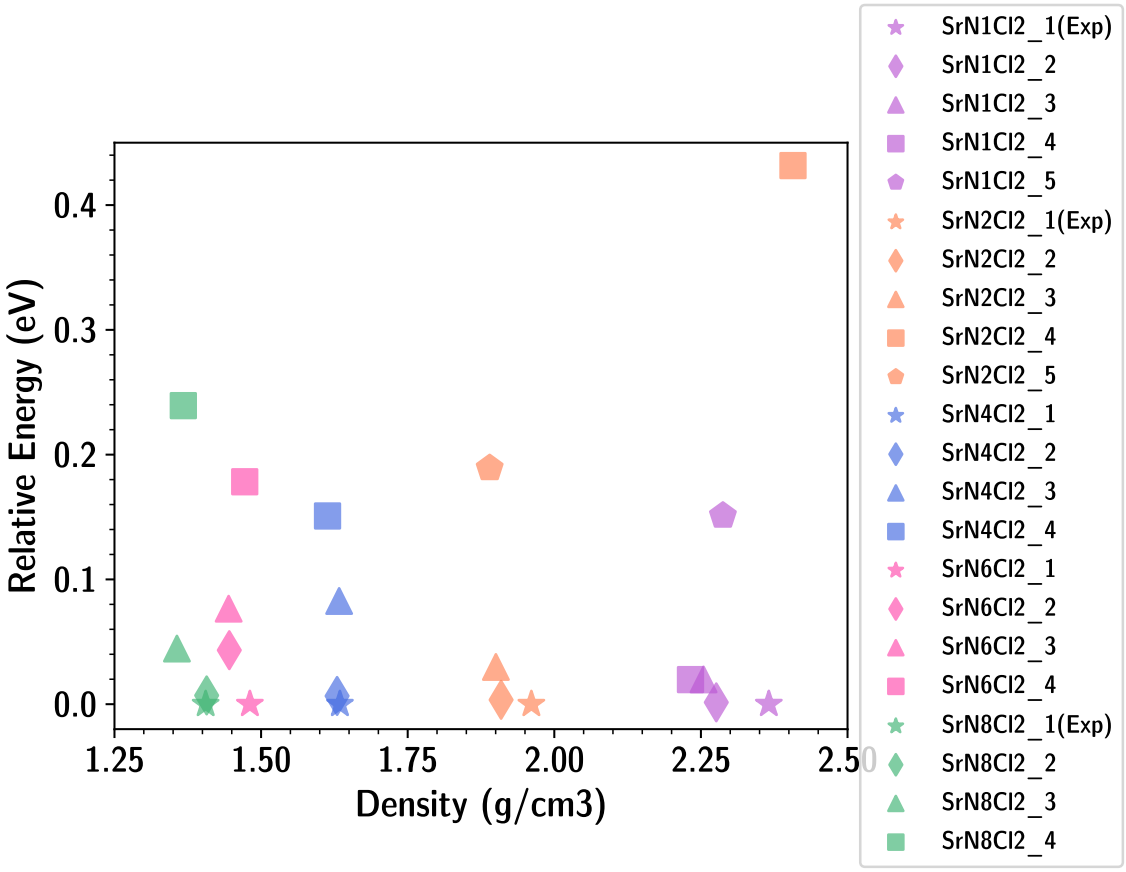
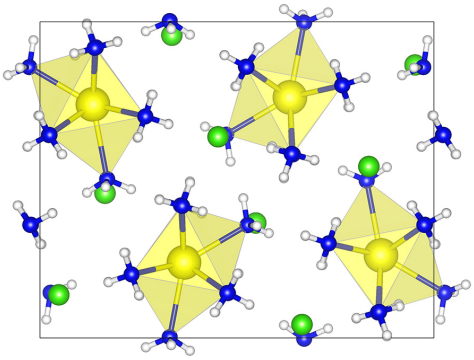


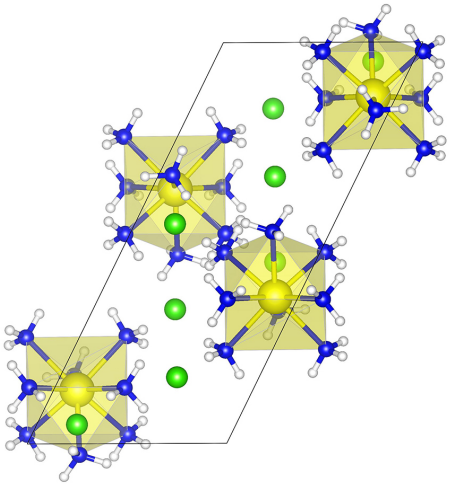
Figure S3: Relative energy-density relationships at PW91-D3 level of calculations for all considered predicted crystal structures.

Table S2: Crystallographic details, energy ranking and density of the stable octamine structures in the energy range up to 0.5 eV/f.u. above the global minimum calculated within the PBE-D3, PBESOL-D3 and PW91-D3 levels of theory.

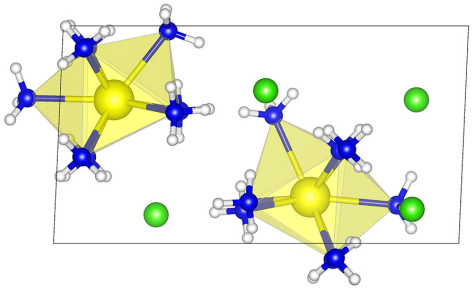
Structure Name		**PBE-D3**	**PBESOL-D3**	**PW91-D3**
SrN8Cl2_1(Exp) $P2_1/c$ (14)	a	7.3965	7.2305	7.5035
	b	14.9465	14.5719	15.1669
	c	11.9658	11.7064	12.2405
	β	90.09	90.09	90.23
	ΔE	0.0	0.0	0.0
	ρ	1.4801	1.5874	1.4055
SrN8Cl2_2 $P2_1/c$ (14)	a	7.4034	7.2366	7.5115
	b	11.9565	11.7049	12.2254
	c	16.6439	16.2241	16.8976
	β	116.25	116.21	116.28
	ΔE	0.0061	0.0043	0.0070
	ρ	1.4818	1.5879	1.4072
SrN8Cl2_3 $P1$ (1)	a	7.0317	6.8543	7.2685
	b	7.4214	7.2621	7.5648
	c	13.0369	12.7612	13.1321
	α	89.45	89.40	89.39
	β	87.63	87.41	88.26
	γ	89.27	89.14	89.54
	ΔE	0.1272	0.1452	0.0446
	ρ	1.4403	1.5430	1.3565
SrN8Cl2_4 $Pnn2$ (34)	a	7.5032	7.3437	7.7484
	b	14.9764	14.8080	14.8303
	c	5.9410	5.7241	6.2300
	ΔE	0.3011	0.2814	0.2392
	ρ	1.4664	1.5727	1.3674



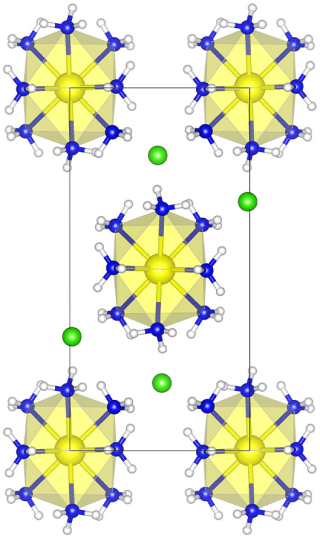
SrN8Cl2_1(Exp)



SrN8Cl2_2

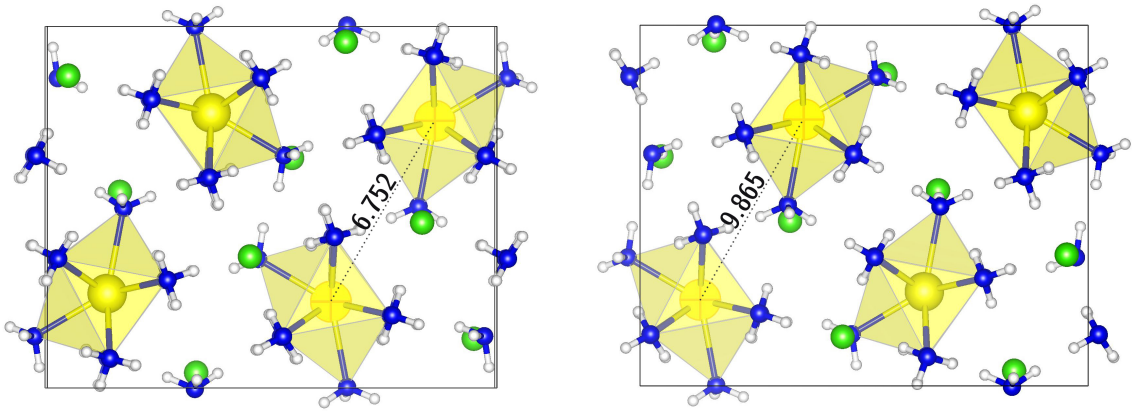


SrN8Cl2_3



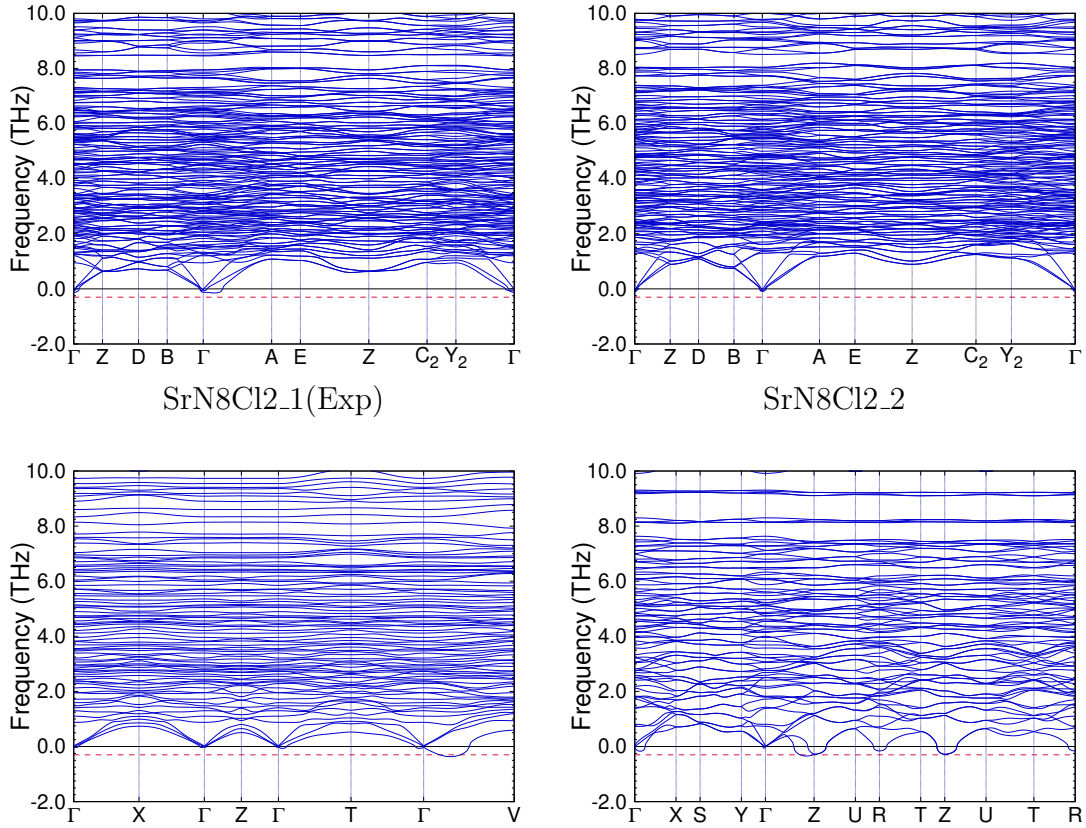
SrN8Cl2_4

Figure S4: Stable octammine crystal structures found by FFCASP.



SrN8Cl2_1(Exp) SrN8Cl2_2

Figure S5: Structural details of two similar octammine structure.



SrN8Cl2_1(Exp) SrN8Cl2_2

SrN8Cl2_3 SrN8Cl2_4

Figure S6: Phonon band diagrams of octammine structures. Dotted red lines indicate the low bounds within the errorbar of 0.3 THz.

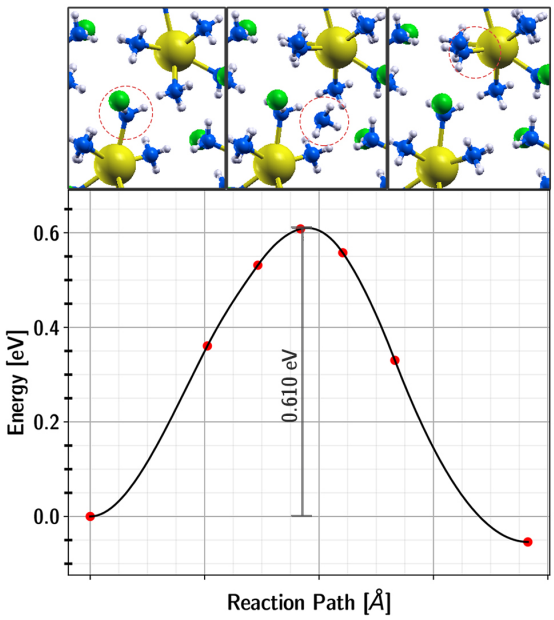
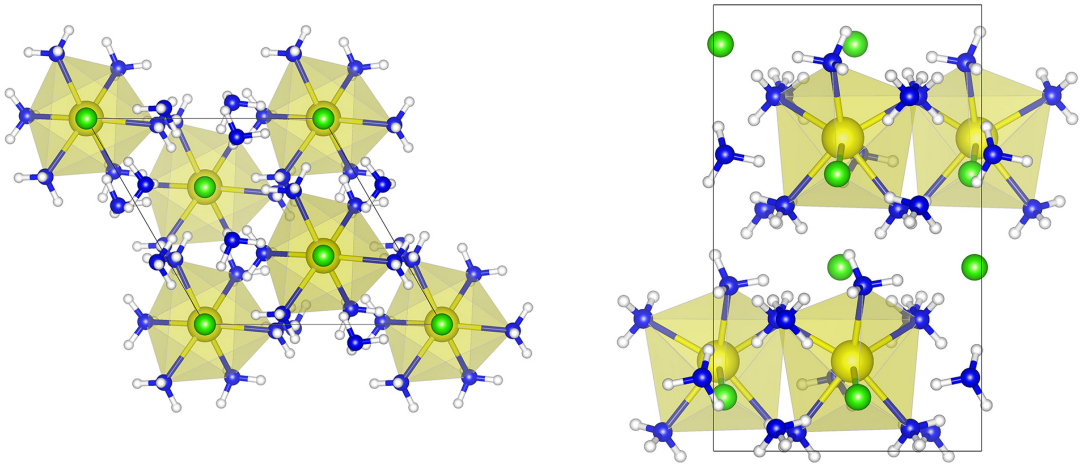
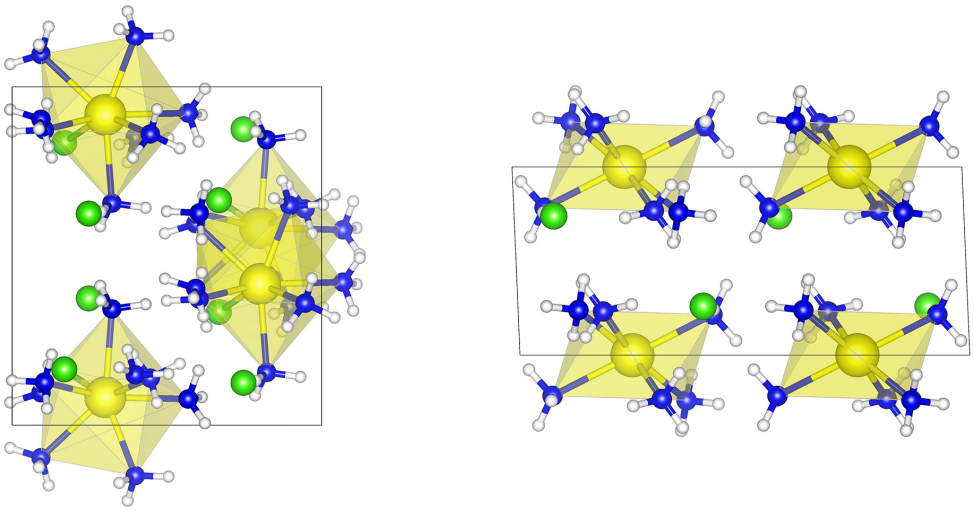


Figure S7: Bulk diffusion NH_3 in SrN8Cl2_1(Exp).



SrN6Cl2_1 SrN6Cl2_2



SrN6Cl2_3 SrN6Cl2_4

Figure S8: Stable hexammine crystal structures found by FFCASP.

Table S3: Crystallographic details, energy ranking and density of the stable hexamine structures in the energy range up to 0.5 eV/f.u. above the global minimum calculated within the PBE-D3, PBESOL-D3 and PW91-D3 levels of theory.

Structure Name		**PBE-D3**	**PBESOL-D3**	**PW91-D3**
SrN6Cl2_1 *R*3 (146)	a	8.6709	8.5267	8.7098
	c	12.5336	11.9874	13.3595
	γ	120.00	120.0	120.00
	ΔE	0.0	0.0	0.0
	ρ	1.5927	1.7214	1.4809
SrN6Cl2_2 *Cc* (9)	a	10.0404	9.8822	10.3062
	b	8.1930	8.0150	8.3643
	c	13.8151	13.4562	14.0916
	β	97.57	97.30	99.36
	ΔE	0.1083	0.1310	0.0433
	ρ	1.5389	1.6384	1.4458
SrN6Cl2_3 *Cc* (9)	a	10.9664	10.7874	11.1949
	b	10.4937	10.3313	10.7203
	c	11.2010	10.8456	11.4177
	β	119.19	119.03	119.06
	ΔE	0.1302	0.1502	0.0765
	ρ	1.5371	1.6380	1.4447
SrN6Cl2_4 *P*2/*c* (13)	a	5.6002	5.4599	5.6811
	b	7.5100	7.4020	7.6934
	c	13.2439	13.0202	13.4607
	β	92.22	92.44	91.38
	ΔE	0.1940	0.2009	0.1783
	ρ	1.5556	1.6469	1.4721

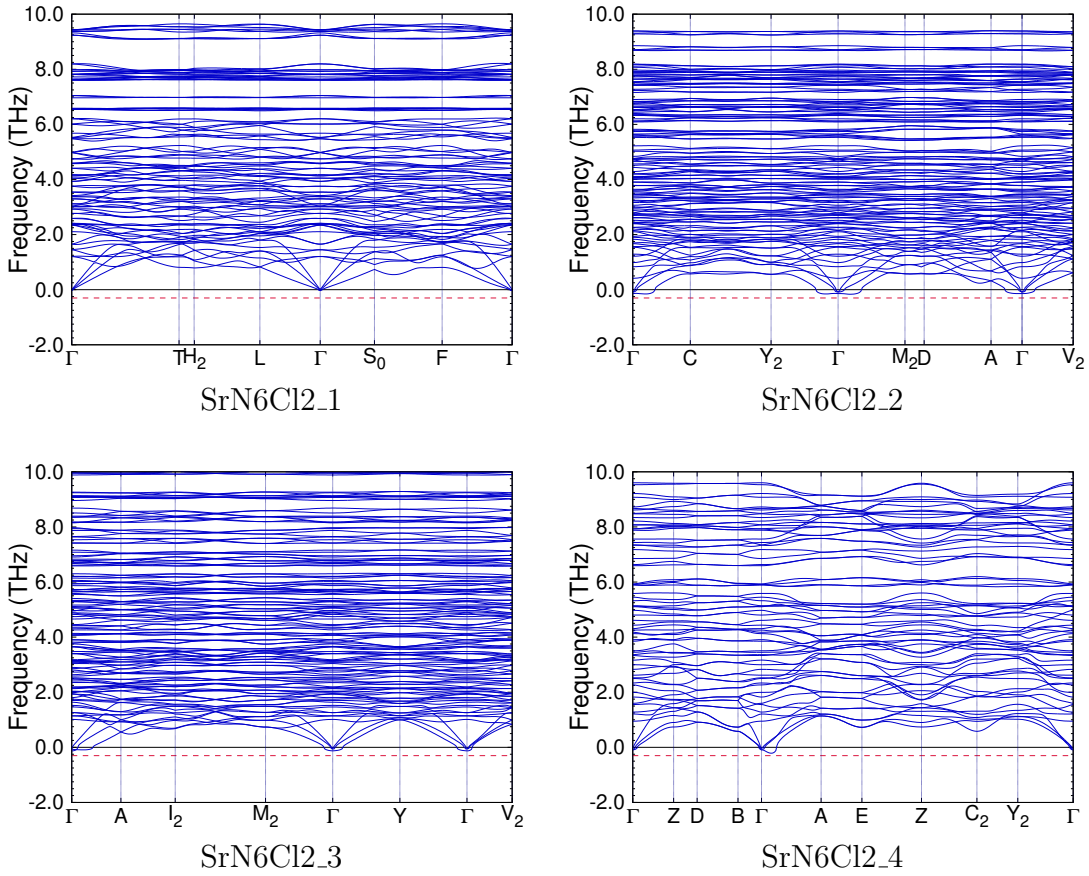
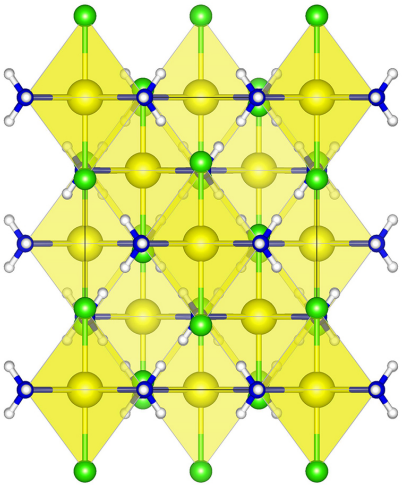
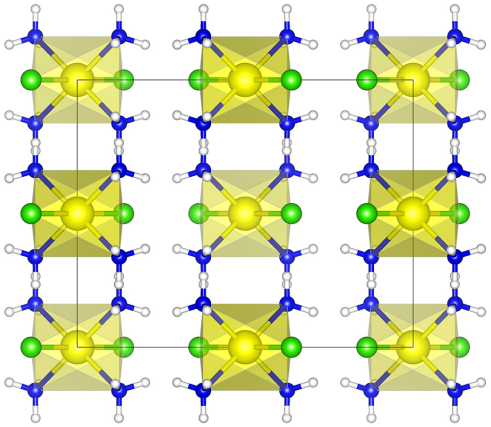


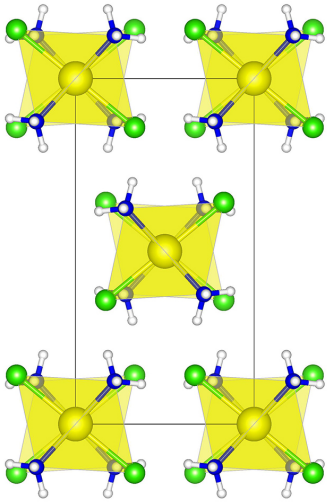
Figure S9: Phonon band diagrams of hexammine structures. Dotted red lines indicate the low bounds within the errorbar of 0.3 THz.



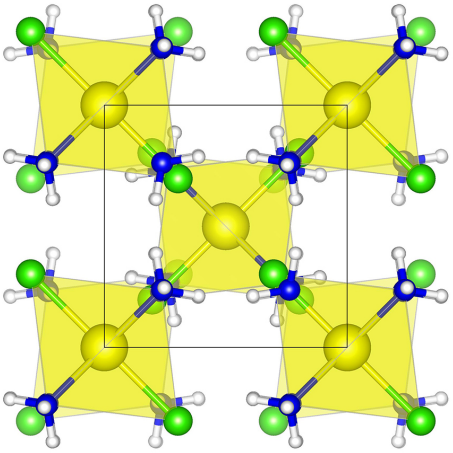
SrN4Cl2_1



SrN4Cl2_2



SrN4Cl2_3



SrN4Cl2_4

Figure S10: Stable tetrammine crystal structures found by FFCASP.

Table S4: Crystallographic details, energy ranking and density of the stable tetramine structures in the energy range up to 0.5 eV/f.u. above the global minimum calculated within the PBE-D3, PBESOL-D3 and PW91-D3 levels of theory.

Structure Name		**PBE-D3**	**PBESOL-D3**	**PW91-D3**
SrN4Cl2_1 *Fddd* (70)	a	8.2846	8.0922	8.5050
	b	10.3188	10.2239	10.4692
	c	20.5038	19.9657	20.6889
	ΔE	0.0	0.0	0.0
	ρ	1.7177	1.8227	1.6344
SrN4Cl2_2 *Cmce* (64)	a	10.2606	10.0032	10.3555
	b	6.6760	6.5978	6.8017
	c	12.8366	12.5547	13.1156
	ΔE	0.0105	0.0126	0.0066
	ρ	1.7120	1.8168	1.6296
SrN4Cl2_3 *Ibam* (72)	a	6.6385	6.5667	6.7326
	b	12.9623	12.7381	13.2248
	c	10.2169	9.9064	10.3529
	ΔE	0.0802	0.0728	0.0827
	ρ	1.7123	1.8167	1.6331
SrN4Cl2_4 $I-42m$ (121)	a	6.6279	6.5164	6.7551
	c	20.2231	19.6910	20.4491
	ΔE	0.1546	0.1688	0.1508
	ρ	1.6946	1.8004	1.6133

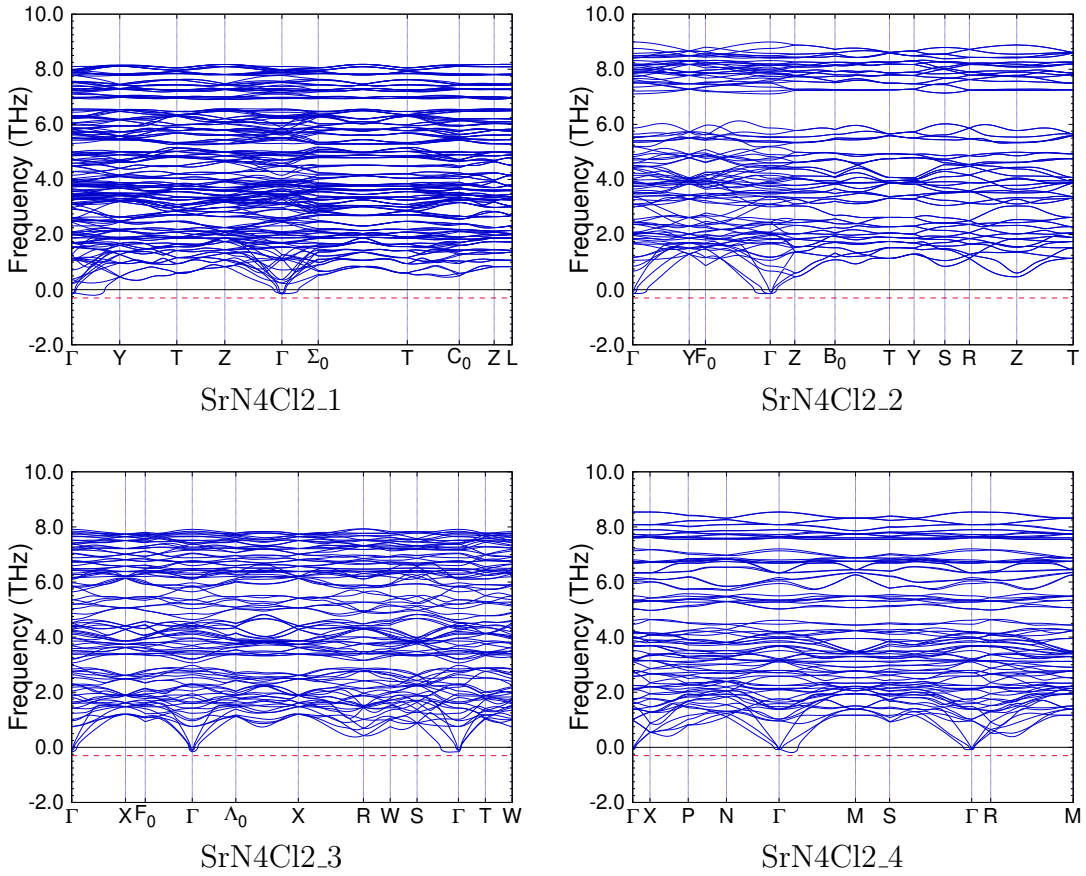
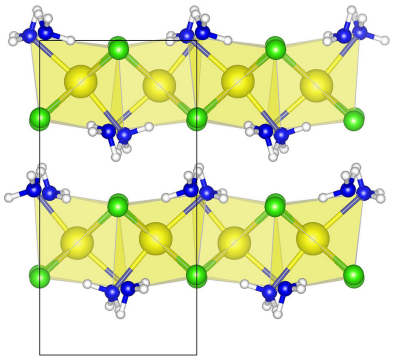
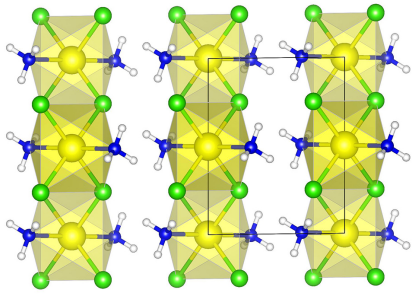


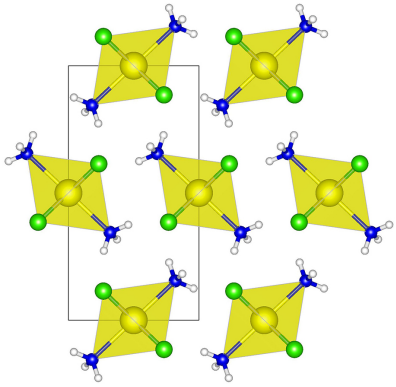
Figure S11: Phonon band diagrams of tetrammine structures. Dotted red lines indicate the low bounds within the errorbar of 0.3 THz.



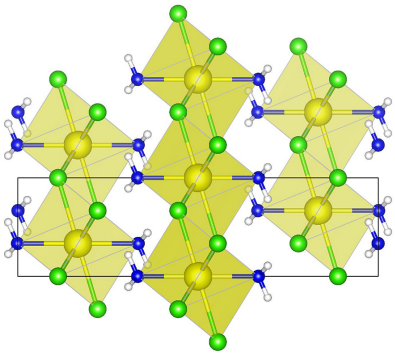
SrN2Cl2_1(Exp)



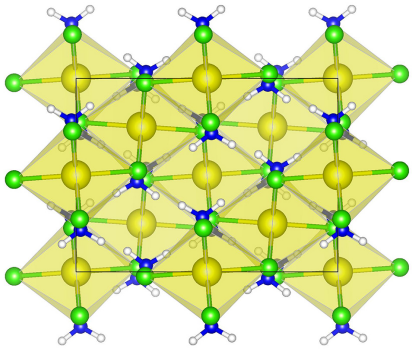
SrN2Cl2_2



SrN2Cl2_3



SrN2Cl2_4

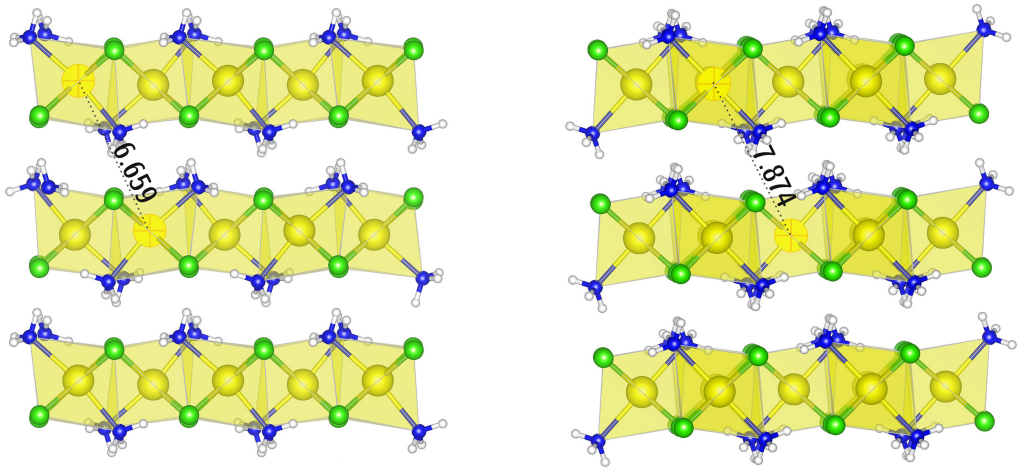


SrN2Cl2_5

Figure S12: Experimental and the predicted stable diammine crystal structures found by FFCASP.

Table S5: Crystallographic details, energy ranking and density of the stable diamine structures in the energy range up to 0.5 eV/f.u. above the global minimum calculated within the PBE-D3, PBESOL-D3 and PW91-D3 levels of theory.

Structure Name		**PBE-D3**	**PBESOL-D3**	**PW91-D3**
SrN2Cl2_1(Exp) Pc (7) ($Z' = 4$)	a	8.1659	8.0647	8.2727
	b	6.1329	5.9964	12.7401
	c	12.3484	12.0279	20.6889
	β	90.09	90.39	91.40
	ΔE	0.0	0.0	0.0
	ρ	2.0684	2.1992	1.9609
SrN2Cl2_2 $P2_1/c$ (14) ($Z' = 2$)	a	6.2674	6.1387	6.5874
	b	6.1704	6.0495	6.1588
	c	8.0809	7.9261	8.2997
	β	90.95	90.64	95.83
	ΔE	0.0246	0.0307	0.0035
	ρ	2.0469	2.1730	1.9093
SrN2Cl2_3 $P2_1/c$ (14) ($Z' = 2$)	a	4.2864	4.2285	4.3213
	b	6.1099	5.9783	6.2063
	c	11.9890	11.6666	12.5683
	β	90.28	90.40	93.21
	ΔE	0.0782	0.0786	0.0298
	ρ	2.0370	2.1687	1.9004
SrN2Cl2_4 $R-3m$ (166) ($Z' = 3$)	a	5.1809	5.0739	5.2174
	c	16.5299	16.0912	16.9070
	γ	120.00	120.00	120.00
	ΔE	0.2363	0.0098	0.4317
	ρ	2.4967	2.6741	2.4070
SrN2Cl2_5 $Fdd2$ (43) ($Z' = 2$)	a	8.3870	8.2161	8.5915
	b	11.3899	11.1249	11.4762
	c	13.5673	13.4044	13.7301
	ΔE	0.2634	0.2259	0.1892
	ρ	1.9739	2.0881	1.8898



SrN2Cl2_1(Exp) SrN2Cl2_2

Figure S13: Structural differences between SrN2Cl2_1(Exp) and SrN2Cl2_2.

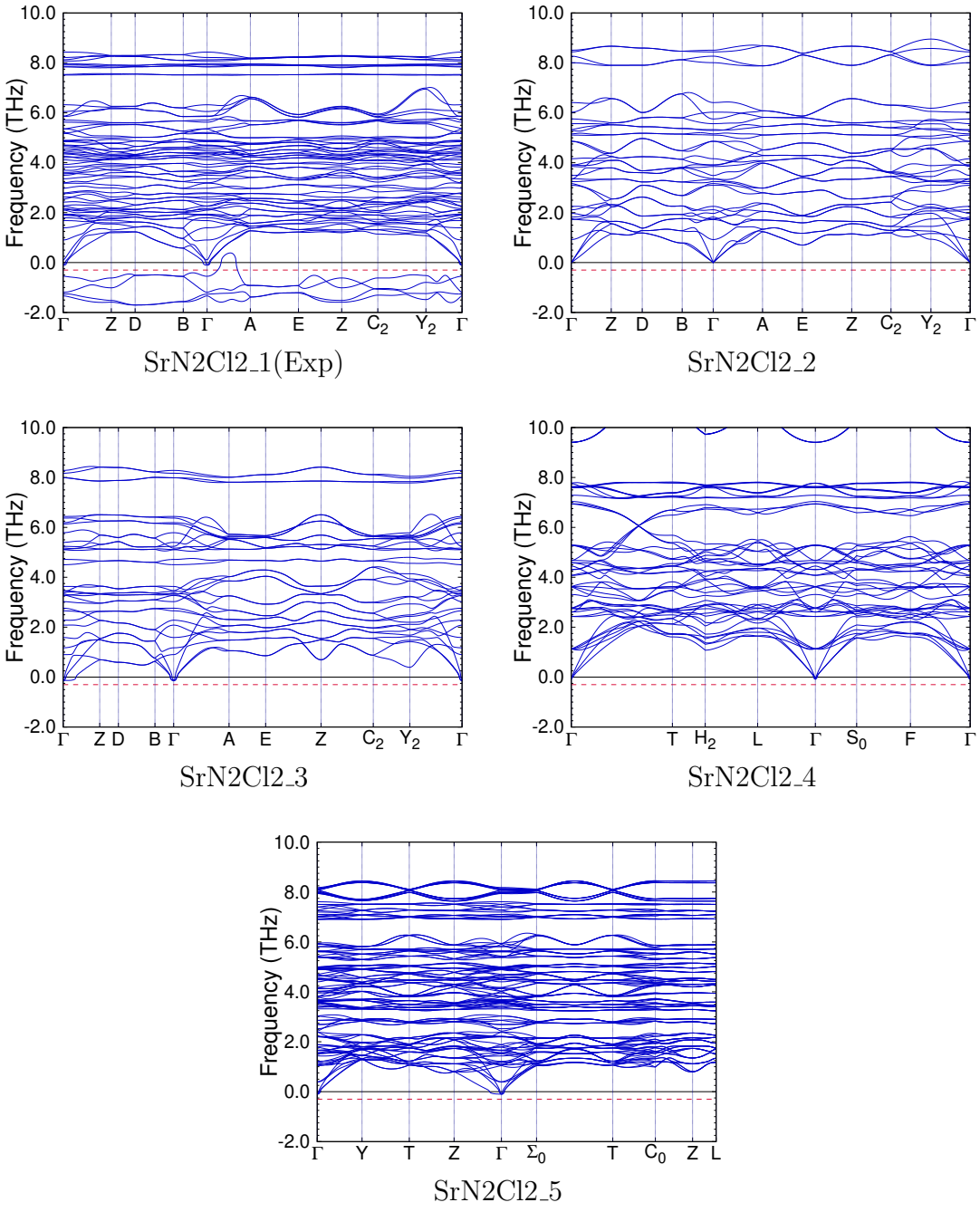


Figure S14: Phonon band diagrams of diammine structures. Dotted red lines indicate the low bounds within the errorbar of 0.3 THz.

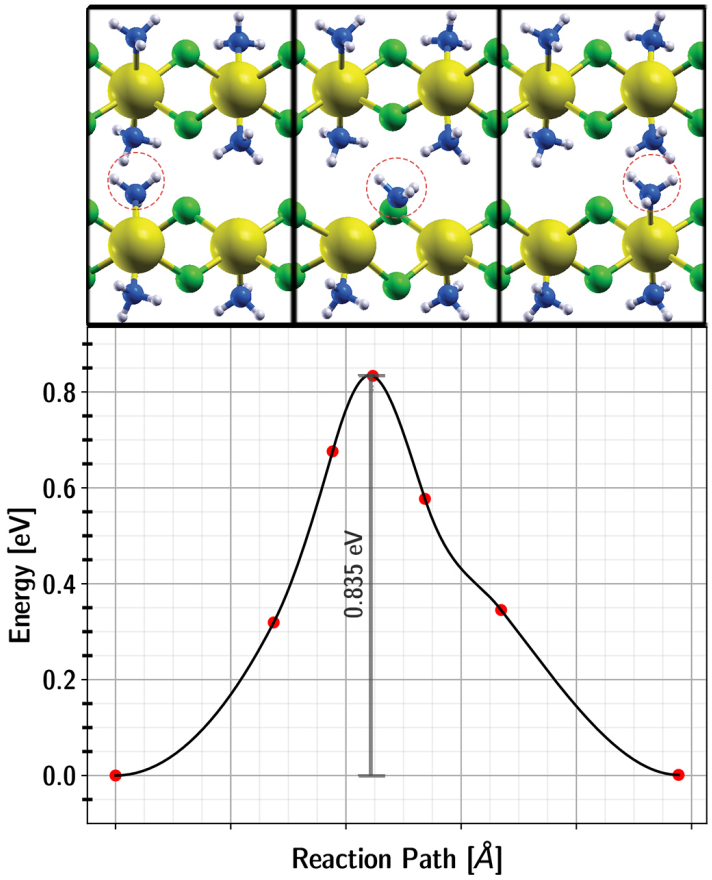


Figure S15: Bulk diffusion of NH_3 in SrN2Cl2_1(Exp).

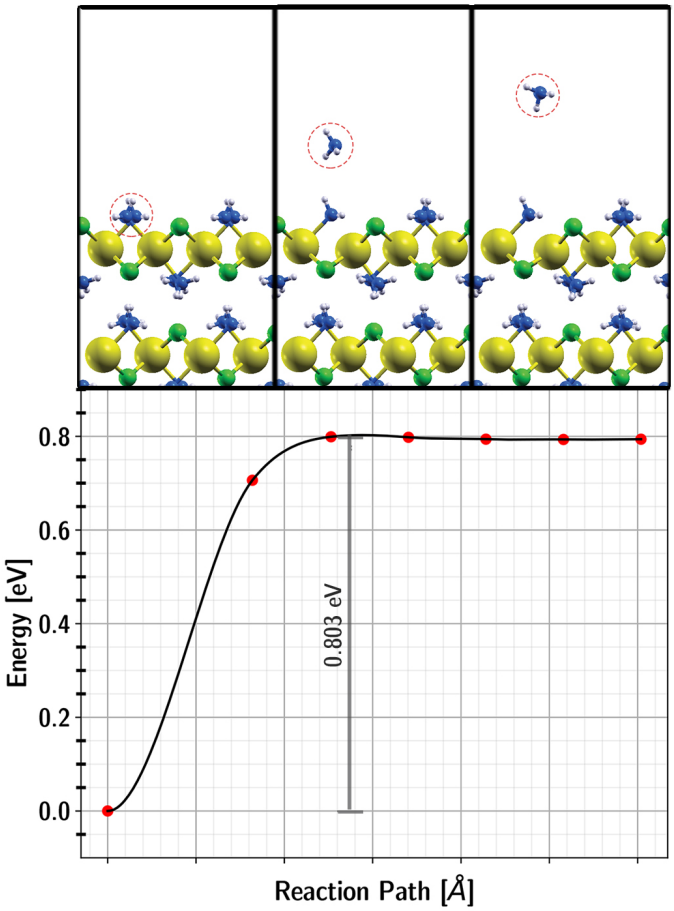


Figure S16: Surface diffusion of NH_3 in SrN2Cl2_1(Exp).

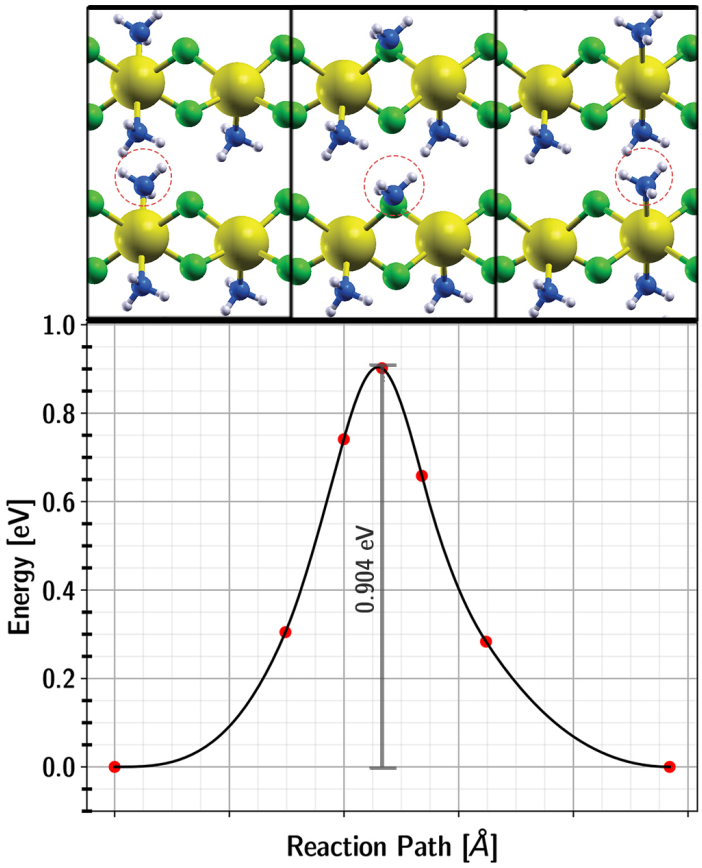
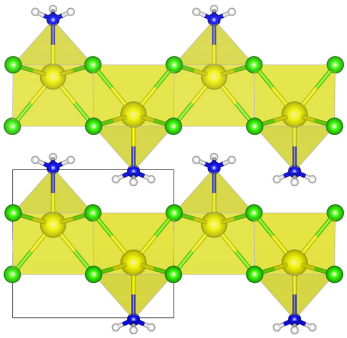
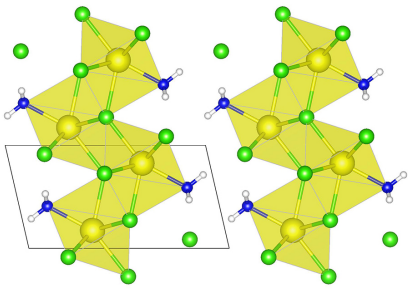


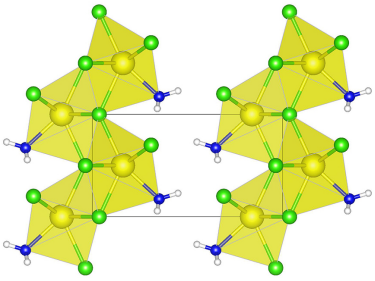
Figure S17: Bulk diffusion of NH_3 in SrN2Cl2_2.



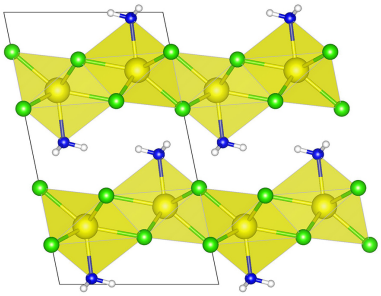
SrN1Cl2_1(Exp)



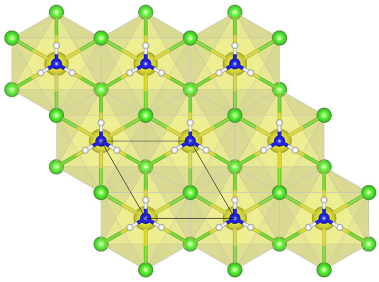
SrN1Cl2_2



SrN1Cl2_3



SrN1Cl2_4



SrN1Cl2_5

Figure S18: Stable monoammine crystal structures found by FFCASP.

Table S6: Crystallographic details, energy ranking and density of the stable monoamine structures in the energy range up to 0.5 eV/f.u. above the global minimum calculated within the PBE-D3, PBESOL-D3 and PW91-D3 levels of theory.

Structure Name		**PBE-D3**	**PBESOL-D3**	**PW91-D3**
SrN1Cl2_1(Exp) $P2_1/m$ (11) ($Z' = 2$)	a	4.5085	4.4399	4.5372
	b	7.5008	7.3576	7.5733
	c	7.3001	7.1227	7.4676
	β	107.78	108.23	106.17
	ΔE	0.0	0.0	0.0
	ρ	2.4802	2.638	2.3658
SrN1Cl2_2 $P2_1/m$ (11) ($Z' = 2$)	a	5.4404	5.3491	5.5129
	b	4.5055	4.4378	4.5394
	c	10.3480	10.1257	10.5550
	β	102.84	102.95	104.14
	ΔE	0.0489	0.0497	0.0015
	ρ	2.3575	2.4889	2.2762
SrN1Cl2_3 $Pmn2_1$ (31) ($Z' = 2$)	a	4.4989	4.4363	4.5316
	b	10.2256	9.9727	10.3336
	c	5.4601	5.3764	5.5225
	ΔE	0.0768	0.0742	0.0198
	ρ	2.3211	2.4511	2.2545
SrN1Cl2_4 $C2/m$ (12) ($Z' = 4$)	a	14.0847	13.7799	14.4199
	b	4.5442	4.4921	4.5790
	c	8.0654	7.8744	8.0800
	β	101.51	101.58	101.73
	ΔE	0.0814	0.0814	0.0197
	ρ	2.3052	2.4419	2.3222
SrN1Cl2_5 $P3m1$ (156) ($Z' = 1$)	a	4.7587	4.6970	4.7788
	c	6.2656	6.0595	6.4437
	γ	120.00	120.00	120.00
	ΔE	0.1867	0.1697	0.1511
	ρ	2.3052	2.5179	2.2875

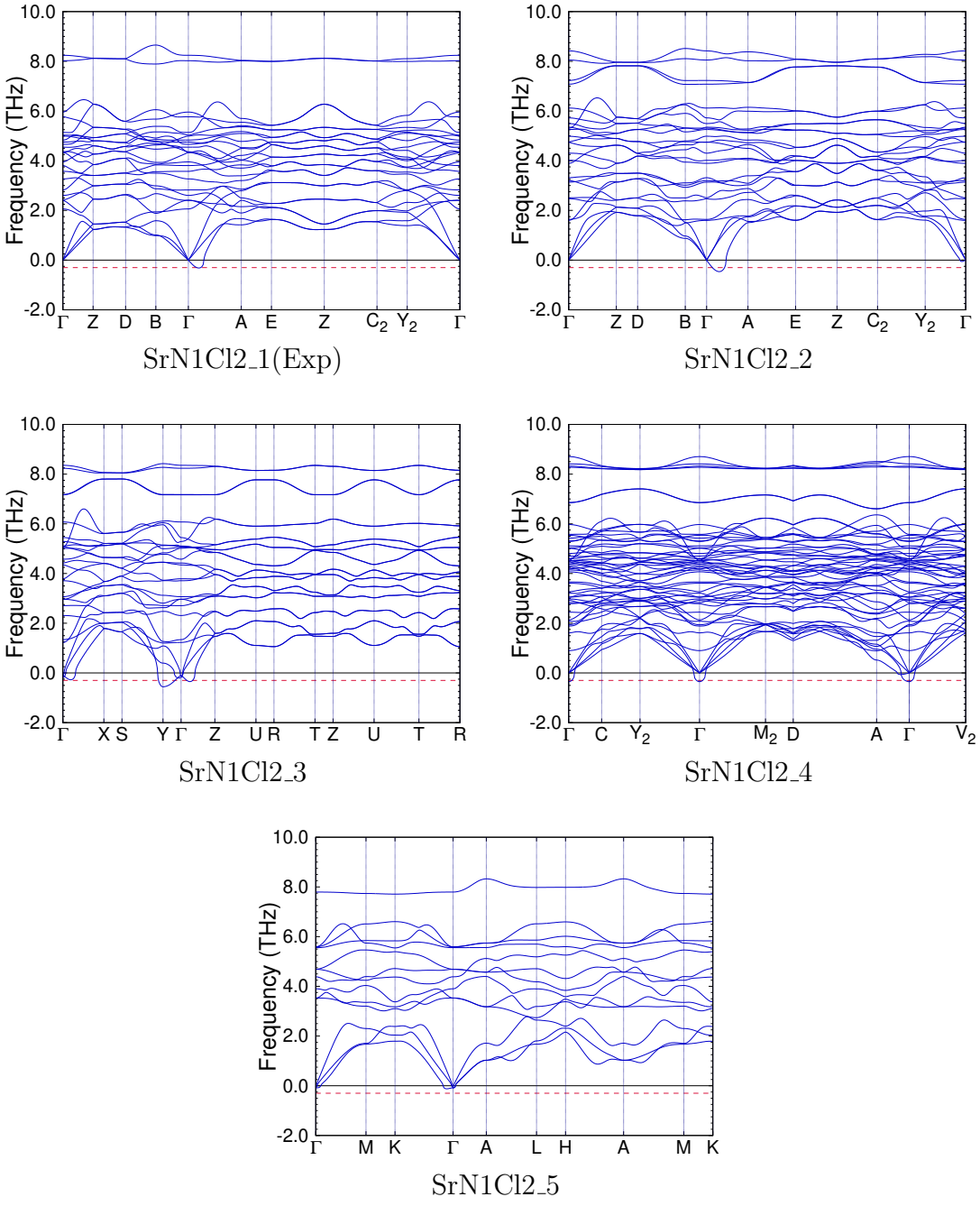


Figure S19: Phonon band diagrams of monoammine structures. Dotted red lines indicate the low bounds within the error bar of 0.3 THz.

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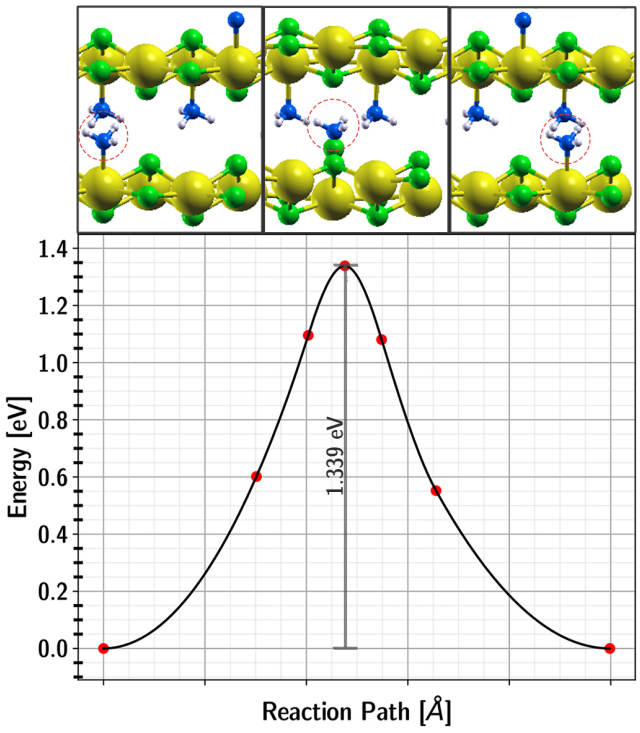

Figure S20: Bulk diffusion of NH_3 in SrN1Cl2_1(Exp).

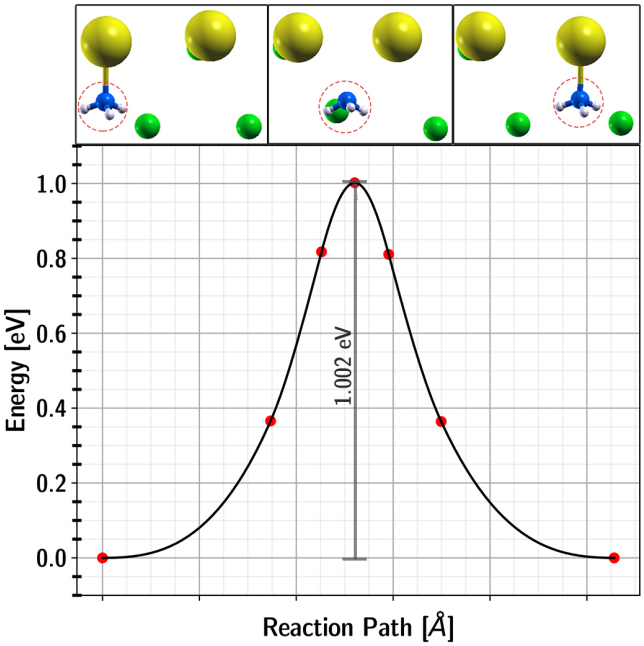

Figure S21: Bulk diffusion of NH_3 in SrN1Cl2_2.