Ordnung muss sein: heteroelement order and disorder in polyoxovanadates

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Content

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Syntheses

General: The purchased chemicals ($NiCl_2 \cdot 6H_2O$, NH_4VO_3, Sb_2O_3 (Merck), GeO_2 (ABCR), diethylenetriamine (Acros), ethylenediamine (Fluka) and phenanthroline (ABCR)) were used without further purifications. The solvothermal reactions of **1** and **2** were performed in DURAN® glass tubes with an inner volume of 11 mL for 7 d at 150 °C. The products consisting of brown crystals were filtered off and washed with water after cooling to room temperature.

*Synthesis of $\{Ni(en)_3\}_3[H_4V_{15}Sb_2Ge_4O_{46}]\cdot en\cdot\approx 10H_2O$ (**1**):*

Compound **1** was obtained by using a solution of 1.7 mL ethylendiamine and 2.3 mL H_2O was given to a mixture of 0.1256 g (1.07 mmol) NH_4VO_3, 0.1234 g (0.423 mmol) Sb_2O_3, 0.0442 g (0.423 mmol) GeO_2 and 0.1251 g (0.526 mmol) $NiCl_2 \cdot 6H_2O$ (pH > 13). Yield based on V was 67 %. Elemental analyses: C 8.00, H 3.25, N 9.92 %; calc. for $C_{20}H_{104}Ge_4N_{20}Ni_3O_{56}Sb_2V_{15}$: C 8.02, H 3.50, N 9.35 %.

EDX ratio: 4.0 (Ge, 16.7 at%) : 3.0 (Ni, 12.5 at%) : 2.0 (Sb, 14.8 at%) : 15.0 (V, 62.5 at%)

*Synthesis of $\{Ni(en)_3\}_3[H_3V_{15}Sb_3Ge_3O_{45}]\cdot\approx 15H_2O$ (**2**):*

A solution of 1.7 mL ethylenediamine and 2.3 mL H_2O were given to a mixture of 0.0944 g (0.800 mmol) NH_4VO_3, 0.0920 g (0.315 mmol) Sb_2O_3, 0.0330 g (0.315 mmol) GeO_2 and 0.0936 g (0.393 mmol) $NiCl_2 \cdot 6H_2O$ (pH > 13) afforded crystallization of **2**. Yield based on V was 88 %. Elemental analyses: C 7.17, H 3.29, N 8.54 %; calc. for $C_{18}H_{105}Ge_3N_{18}Ni_3O_{60}Sb_3V_{15}$: C 7.07, H 3.46, N 8.25 %.

EDX ratio: 3.0 (Ge, 12.5 at%) : 3.0 (Ni, 12.5 at%) : 3.0 (Sb, 12.5 at%) : 15.0 (V, 62.5 at%)

*Synthesis of $\{Ni(en_3)\}_3[V_{15}Ge_3Sb_3O_{45}]\cdot\approx 9H_2O$ (**3**)*

Compound **3** was obtained using the precursor compound $\{Ni(en)_3\}_3[V_{15}Sb_6O_{42}(H_2O)_x]\cdot ca.15H_2O$ (**4**). **4** was synthesized using the published protocol.[ii] 0.1461 g (0.048 mmol) of the precursor compound **4** were mixed with 0.0222 g (0.212 mmol) GeO_2 (Fluka) and a solution of 3.9 mL dist. water and 0.1 mL ethylenediamine (pH ≈ 11). The mixture was heated for 24 h at 150°C. The product was washed with dist. water and ethanol. The brown crystals have been cleaned by sonication in ethanol. Yield based on V: 46 %. Elemental analyses: C 7.00, H 3.00, N 7.92 %; calc. for $C_{18}H_{101}Ge_3N_{18}Ni_3O_{58}Sb_3V_{15}$: C 7.16, H 3.37, N 8.34 %.

EDX ratio: 3.0 (Ge, 12.3 at%) : 3.3 (Ni, 13.1 at%) : 3.6 (Sb, 14.8 at%) : 14.6 (V, 59.8 at%)

Characterization Methods

X-ray powder patterns were recorded on a STOE Stadi-P powder diffractometer with a Ge monochromator with $Cu_{K\alpha1}$ radiation and a Mythen 1k detector.

A EURO EA elemental analyzer of EURO VECTOR instruments was used for elemental analysis.

DTA-TG measurements were done in Al_2O_3 crucibles with a Netzsch STA 409 CD under a nitrogen flow of 75 mL min^{-1} at a heating rate of 4K min^{-1}.

A Philips Environmental Scanning Electron Microscope ESEM XL30 equipped with an EDX detector enabled investigations for energy dispersive X-ray analyses (EDX).

A Genesis FTIRTM spectrometer from ATI Mattson was used for collecting IR spectra in the range from 400 to 4000 cm^{-1}.

Magnetic data of **1-3** were collected using a Quantum Design MPMS-5XL SQUID magnetometer. Samples were compacted and immobilized into cylindrical PTFE capsules. Temperature-dependent data were recorded in the range 2.0 – 290 K at 0.1 T, and field dependent data in the range 0 – 5.0 T at 2.0 K. The data were corrected for the diamagnetic contributions of both the sample holders and the compounds ($\chi_{m,dia}$ / 10^{-3} cm^3 mol^{-1} = –1.50 (**I**), –1.53 (**II**), –1.88 (**III**)).

Tab. S 1: EDX Data of compounds **1-3**.

	V [at%]	**Sb [at%]**	**Ge [at%]**	**Ni [at%]**
$[V_{15}Sb_2Ge_4Ni_3]$ (1)	62.51	8.33	16.66	12.50
$[V_{15}Sb_3Ge_3Ni_3]$ (2)	62.51	12.50	12.50	12.50
$[V_{15}Sb_3Ge_3Ni_2]$ (3)	59.80	14.80	12.30	13.10

Tab. S 2: BVS calculations for determination of the oxidations state of V for compounds **1-3** With b = 0.37 and R0 for V-O = 1.773.[1]

$\{Ni(en)_3\}_3[H_4V_{15}Sb_2Ge_4O_{46}] \cdot en$ (I)

	distances	exp[(R0-R)/b]
V(1)-O	1.613	1.54
	1.916	0.68
	1.934	0.65
	1.968	0.59
	2.008	0.53
		3.99
V(2)-O	1.621	1.51
	1.914	0.68
	1.916	0.68
	1.973	0.58
	1.982	0.57
		4.02
V(3)-O	1.607	1.57
	1.923	0.67
	1.941	0.64
	1.959	0.60
	2.019	0.51
		3.99
V(4)-O	1.612	1.55
	1.913	0.68
	1.944	0.63
	1.959	0.60
	2.003	0.54
		4.00
V(5)-O	1.607	1.57
	1.929	0.66
	1.943	0.63
	1.966	0.59
	1.997	0.55
		3.99
V(6)-O	1.607	1.57
	1.91	0.69
	1.941	0.64
	1.992	0.55
	2.005	0.53
		3.98

$\{Ni(en)_3\}_3[H_3V_{15}Sb_3Ge_3O_{45}]$ (II)

	distances	exp[(R0-R)/b]
V(1)-O	1.62	1.53
	1.94	0.64
	1.94	0.64
	1.95	0.61
	2.00	0.54
		3.97
V(2)-O	1.61	1.55
	1.93	0.66
	1.94	0.64
	2.01	0.52
	1.98	0.57
		3.93
V(3)-O	1.61	1.54
	1.92	0.67
	1.94	0.63
	1.94	0.63
	1.98	0.57
		4.04
V(4)-O	1.63	1.48
	1.91	0.69
	1.94	0.64
	1.97	0.58
	1.99	0.55
		3.95
V(5)-O	1.61	1.56
	1.92	0.68
	1.94	0.64
	1.98	0.57
	1.99	0.56
		4.02
V(6)-O	1.62	1.53
	1.92	0.67
	1.92	0.66
	1.99	0.56
	1.99	0.56
		3.98

$\{Ni(en)_3\}_3[H_3V_{15}Sb_3Ge_3O_{45}]$ (III)

	distances	exp[(R0-R)/b]
V(1)-O	1.615	1.53
	1.948	0.62
	1.954	0.61
	1.958	0.61
	2.001	0.54
		3.92
V(2)-O	1.603	1.58
	1.925	0.66
	1.932	0.65
	1.955	0.61
	2.011	0.53
		4.03
V(3)-O	1.606	1.57
	1.927	0.66
	1.932	0.65
	1.965	0.60
	2.002	0.54
		4.01
V(4)-O	1.596	1.61
	1.91	0.69
	1.947	0.62
	1.974	0.58
	2.016	0.52
		4.03
V(5)-O	1.603	1.58
	1.911	0.69
	1.954	0.61
	1.954	0.61
	2.015	0.52
		4.02
V(6)-O	1.608	1.56
	1.922	0.67
	1.95	0.62
	1.976	0.58
	2.006	0.53
		3.96

V(7)-O	1.609	1.56
	1.936	0.64
	1.936	0.64
	1.943	0.63
	2.025	0.51
		3.98

V(7)-O	1.62	1.51
	1.92	0.67
	1.93	0.65
	1.95	0.61
	2.01	0.53
		3.97

V(7)-O	1.597	1.61
	1.925	0.66
	1.934	0.65
	1.978	0.57
	1.979	0.57
		4.07

V(8)-O	1.609	1.56
	1.909	0.69
	1.941	0.64
	1.98	0.57
	2.007	0.53
		3.99

V(8)-O	1.61	1.56
	1.93	0.66
	1.93	0.66
	2.00	0.55
	2.00	0.55
		3.98

V(8)-O	1.607	1.57
	1.922	0.67
	1.937	0.64
	1.948	0.62
	2.006	0.53
		4.03

V(9)-O	1.611	1.55
	1.935	0.65
	1.944	0.63
	1.952	0.62
	2.021	0.51
		3.95

V(9)-O	1.607	1.57
	1.939	0.64
	1.943	0.63
	1.943	0.63
	1.998	0.54
		4.01

V(10)-O	1.621	1.51
	1.91	0.69
	1.932	0.65
	1.953	0.61
	1.988	0.56
		4.02

V(10)-O	1.616	1.53
	1.896	0.72
	1.921	0.67
	1.966	0.59
	1.998	0.54
		4.05

V(11)-O	1.597	1.61
	1.936	0.64
	1.936	0.64
	1.986	0.56
	1.997	0.55
		4.00

V(11)-O	1.605	1.57
	1.927	0.66
	1.945	0.63
	1.973	0.58
	1.999	0.54
		3.99

V(12)-O	1.608	1.56
	1.936	0.64
	1.936	0.64
	1.964	0.60
	2.022	0.51
		3.96

V(12)-O	1.625	1.49
	1.909	0.69
	1.953	0.61
	1.954	0.61
	2.024	0.51
		3.92

V(13)-O	1.62	1.51
	1.916	0.68
	1.936	0.64
	1.972	0.58
	1.997	0.55
		3.97

V(13)-O	1.608	1.56
	1.912	0.69
	1.917	0.68
	1.989	0.56
	2.012	0.52
		4.01

V(14)-O	1.624	1.50
	1.929	0.66
	1.935	0.65
	1.957	0.61
	1.994	0.55
		3.96

V(14)-O	1.606	1.57
	1.93	0.65
	1.949	0.62
	1.95	0.62
	2.028	0.50
		3.97

V(15)-O	1.611	1.55
	1.909	0.69
	1.952	0.62
	1.978	0.57
	2	0.54
		3.97

V(15)-O	1.61	1.55
	1.924	0.66
	1.934	0.65
	1.958	0.61
	1.962	0.60
		4.07

Tab. S 3: BVS calculations for determination of the oxidations state of the O-H groups for compounds **1-3** with b = 0.94 and R0 for O-H = 0.569. [i]

$\{Ni(en)_3\}_3[H_4V_{15}Sb_2Ge_4O_{46}] \cdot en$ (I)

	distances	*exp[(R0-R)/b]*
O(4)-X	1.701	1.22
	0.7	0.87
		2.09
O(11)-X	1.733	1.12
	0.7	0.87
		1.99
O(18)-X	1.65	1.40
	0.7	0.87
		2.27
O(14)-X	1.546	1.86
	0.7	0.87
		2.73

$\{Ni(en)_3\}_3[H_3V_{15}Sb_3Ge_3O_{45}]$ (II)

	distances	*exp[(R0-R)/b]*
O(1)-X	1.712	1.19
	0.7	0.87
		2.06
O(2)-X	1.731	1.13
	0.7	0.87
		2.00
O(3)-X	1.692	1.25
	0.7	0.87
		2.12

$\{Ni(en)_3\}_3[H_3V_{15}Sb_3Ge_3O_{45}]$ (III)

	distances	*exp[(R0-R)/b]*
O(6)-X	1.657	1.38
	0.7	0.87
		2.25
O(12)-X	1.637	1.45
	0.7	0.87
		2.32
O(18)-X	1.672	1.32
	0.7	0.87
		2.19

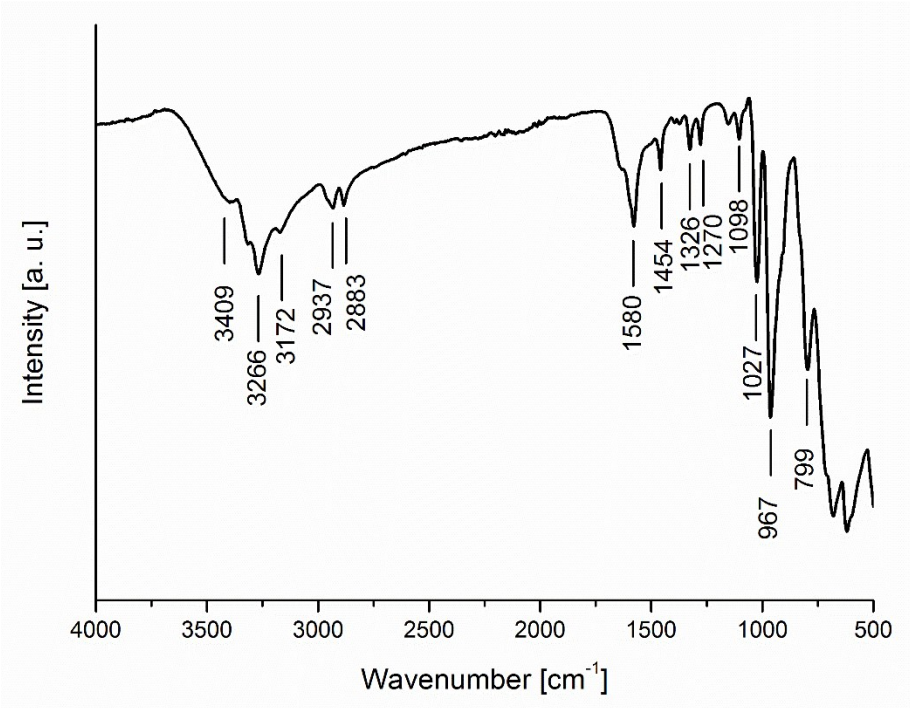


Fig. S 1: IR spectrum of compound **1**.

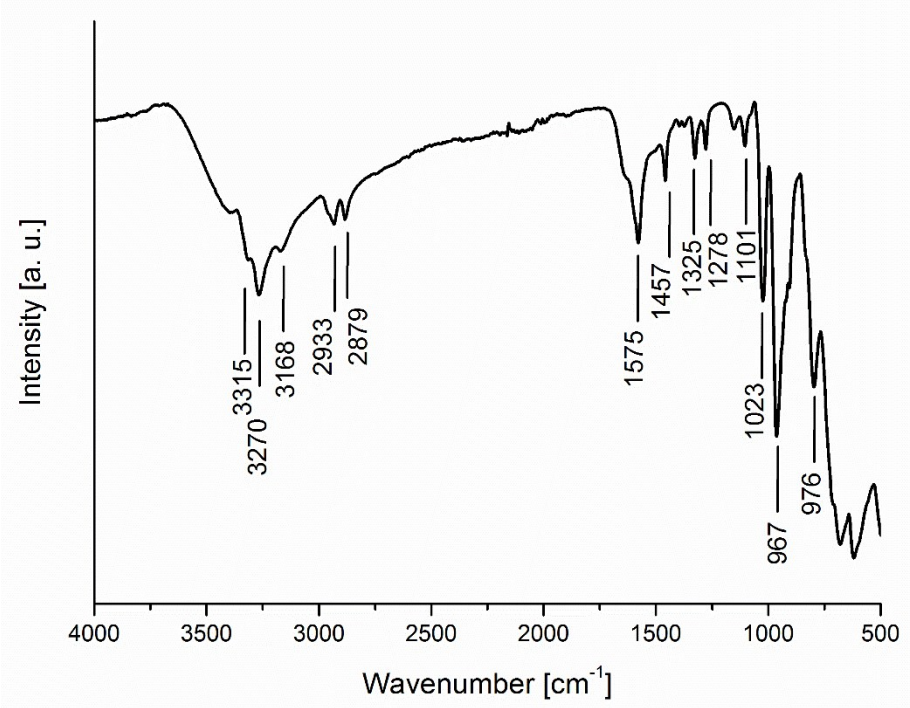


Fig. S 2: IR spectrum of compound **2**.

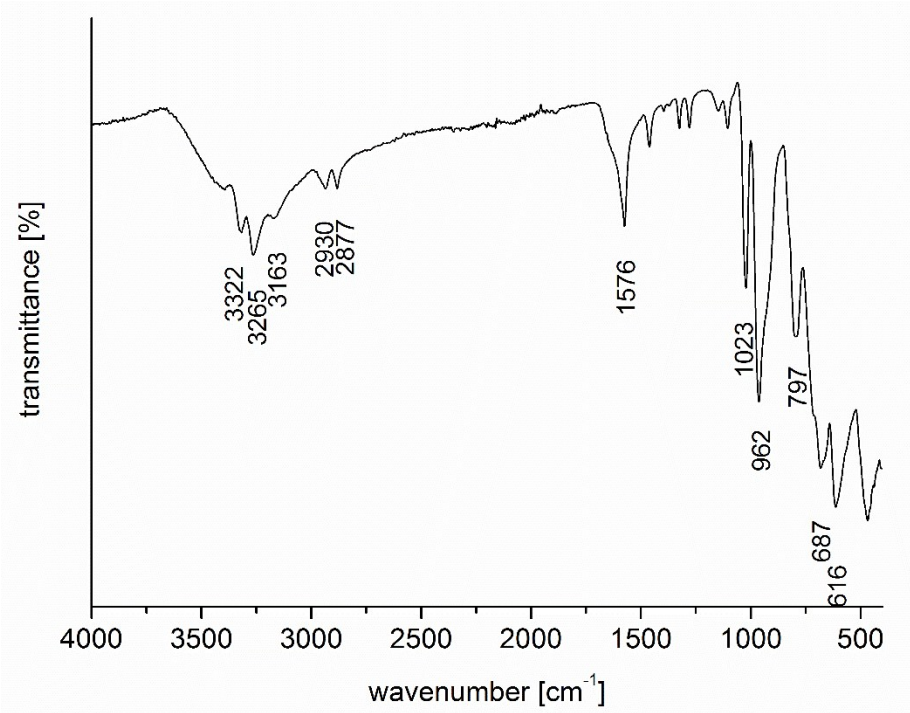


Fig. S 3: IR spectrum of compound **3**.

Tab. S 4: Selected data of data acquisition and crystal structure refinement results for **1-3**.

	1	**2**	**3**
Formula	$C_{20}H_{84}Ge_4N_{20}Ni_3O_{46}Sb_2V_{15}$	$C_{18}H_{75}Ge_3N_{18}Ni_3O_{45}Sb_3V_{15}$	$C_{18}H_{93}Ge_3N_{18}Ni_3O_{54}Sb_3V_{15}$
MW / g·mol^{-1}	2815.16	2787.21	2949.35
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$C2$	$P2_1$
***a* /Å**	12.6027(7)	18.1983(12)	14.9473(3)
***b* / Å**	26.4698(17)	22.7116(15)	18.8080(3)
***c* / Å**	15.1116(9)	14.4488(10)	16.1556(3)
***α* / °**	90	90	90
***β* / °**	114.801(6)	126.600(6)	112.6160(10)
***γ* / °**	90	90	90
***V* / Å^3**	4576.2(5)	4794.3(6)	4192.55(14)
***T* / K**	200	200	170
Z	2	2	2
***Density* / Mg/m^3**	2.043	1.931	2.336
***μ* / mm^{-1}**	4.005	3.787	4.343
θ_{max} / °	26.98	27.996	28.003
measured refl.	32887	29983	51412
unique refl.	19699	11322	17911
R_{int}	0.0292	0.0563	0.0568
refl. with $F_0>4\sigma(F_0)$	18236	10041	16811
Parameters	1003	512	1104
$R_1[F_0>4\sigma(F_0)]$	0.0344	0.0314	0.0469
wR_2 (all refl.)	0.0873	0.0775	0.1181
GOF	1.037	0.996	1.025
$\Delta\rho_{max/min}$ /e·Å^{-3}	1.830, -1.833	0.721, -0.690	2.251/-1.978
Flack x parameter	-	0.017(8)	-
BASF parameter	0.038(11)	-	0.12(2)

Single crystal X-ray analysis

The data were measured using an Imaging Plate Diffraction System (IPDS-2) from STOE, Germany with MoKα-radiation. For all compounds a numerical absorption correction was performed. The structure were solved with SHELXT and refined using SHELXL-2014. All non-hydrogen atoms, except the O atoms of lower occupancy connected to the Ge atoms in **1** and **2** were refined anisotropic. The C-H and N-H H atoms were positioned with idealized geometry and refined isotropic with $U_{iso}(H) = 1.2U_{eq}(C)$ using a riding model. In all compounds the O-H H atoms were not located but considered in the calculation of the formula and the molecular mass. In compound **3**, some of the ethylenediamine molecules are disordered and were refined using a split model. For this compound the Flack-x parameter is close to 0, but not within the estimated standard deviation. Therefore, a twin-refinement was performed, which was also performed for compound **1**. In compound **1** and **2**, some of the Ge and Sb atoms occupy the same crystallographic positions. In the

beginning the site occupation factor was refined but finally it was fixed to the refined values. In both of these compounds there are also additional water molecules that are disordered and for which no reasonable structure model was found. Therefore, the data were corrected for disordered solvent using the Squeeze option in Platon. For compound **1** a void volume of 824.5 Å^3 is calculated which can host ≈ 10 H_2O molecules per formula unit. For **2**, the calculated void space is 1202 Å^3 which is large enough for 15 water molecules per formula unit.

CCDC 1503959 (Compound **1**), CCDC 1503958 (Compound **2**) and CCDC 1820425 (Compound **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

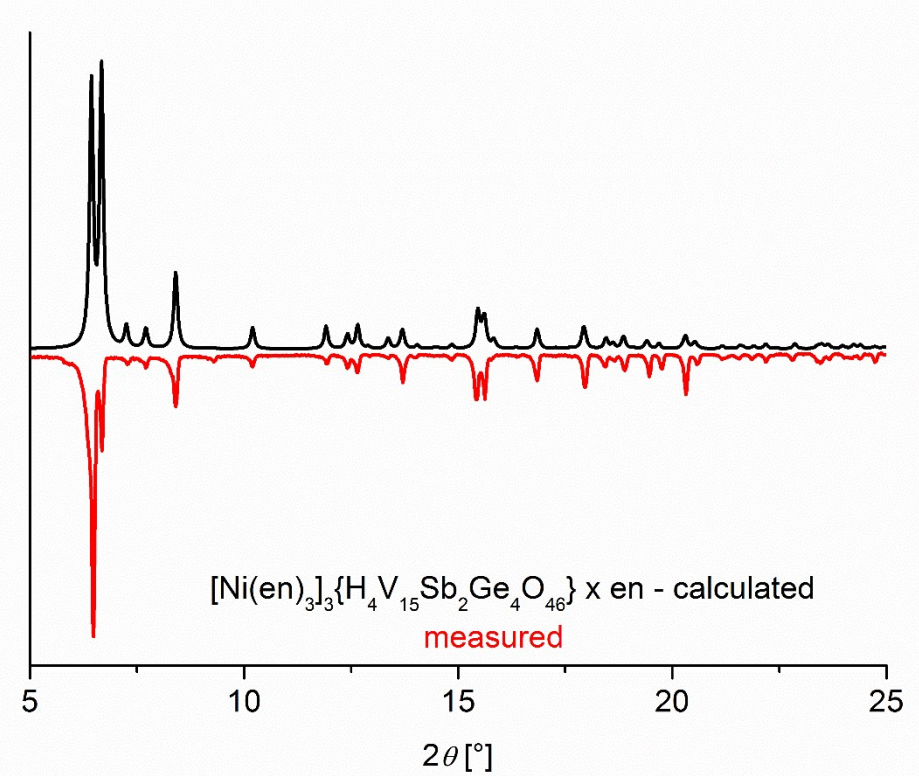


Fig. S 4: Powder pattern of compound **1** compared with calculated Data.

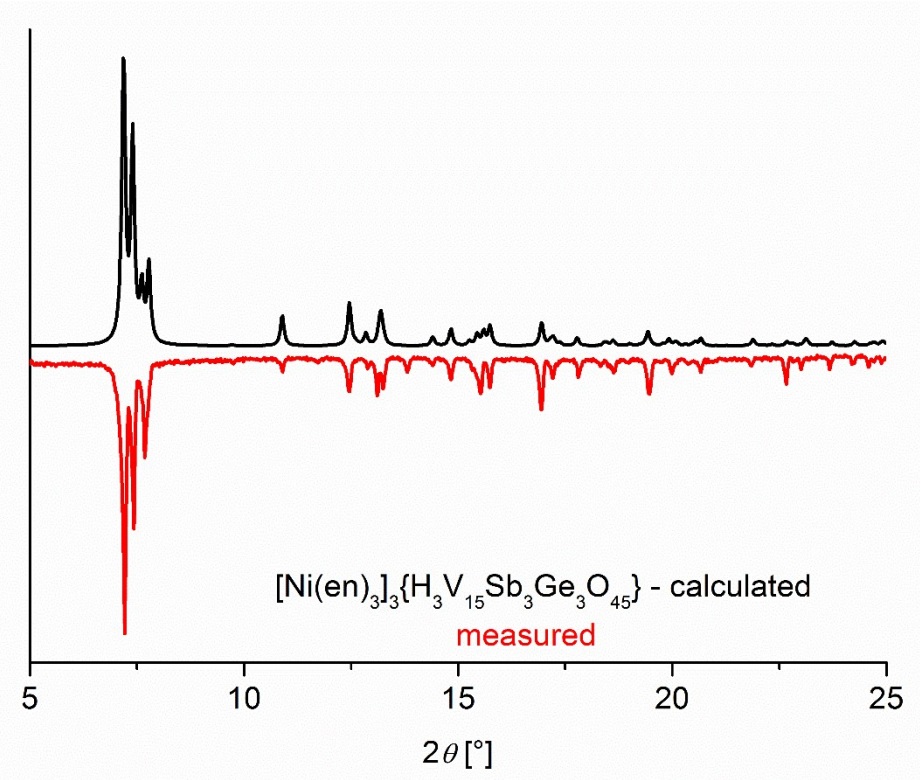


Fig. S 5: Powder pattern of compound **2** compared with calculated Data.

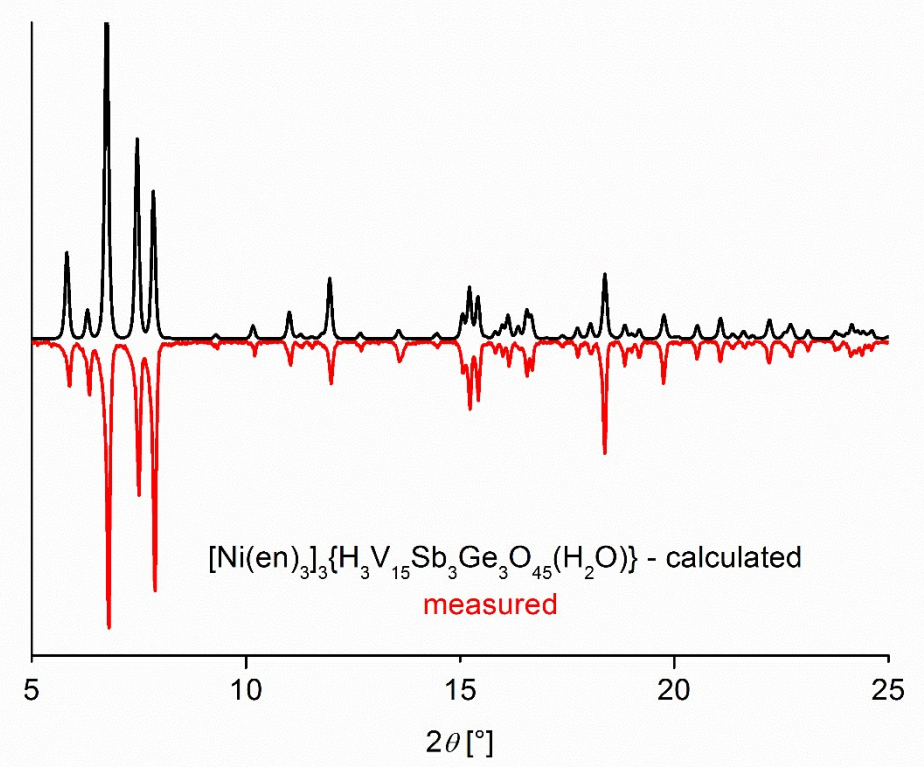


Fig. S 6: Powder pattern of compound **3** compared with calculated Data.

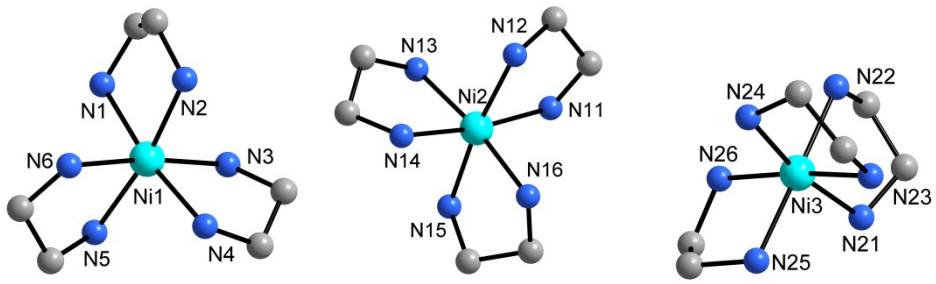


Fig. S 7: View of the three different $[Ni(en)_3]^{2+}$ complexes in compound **1**; all of the complexes are Λ-isomers. Grey spheres represent C atoms; H atoms are omitted for clarity.

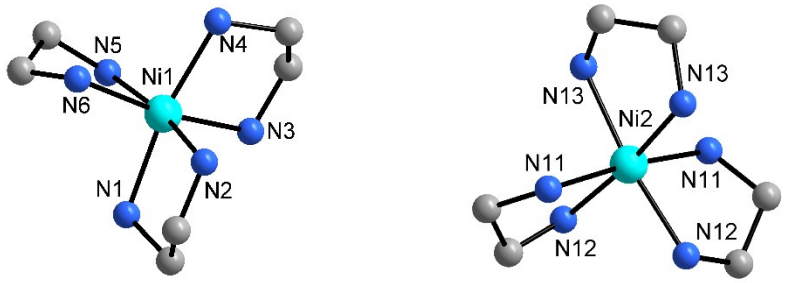


Fig. S 8: The two isomeric structures of $[Ni(en)_3]^{2+}$ of compound **2**: left: Δ-isomer, right: Λ- isomer. Grey: C atoms; H atoms are omitted for clarity. Only selected atoms are labeled.

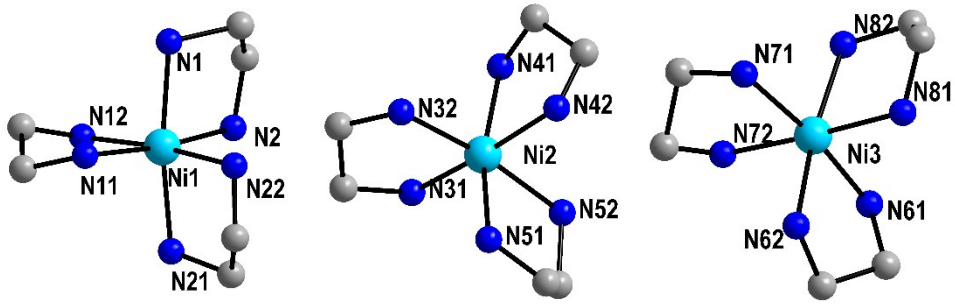
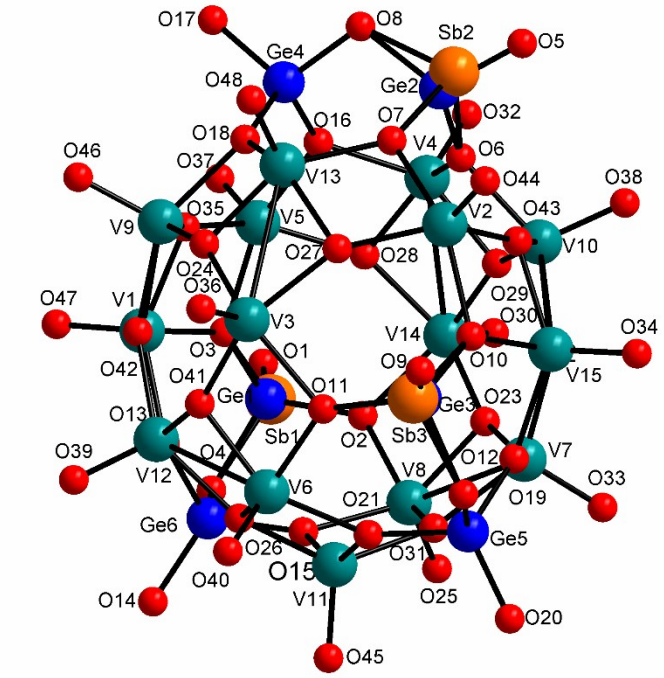


Fig. S 9: View of the three different $[Ni(en)_3]^{2+}$ complexes in compound **3**; Ni(1) is a Δ-isomer and Ni(2) and Ni(3) are Λ-isomers. Grey: C atoms; H atoms are omitted for clarity. Only selected atoms are labeled.

Tab. S 5: Selected bond lengths [Å] for the anion in compound **1**.



Sb(1)-O(2)	1.966(5)	V(5)-O(37)	1.613(6)
Sb(1)-O(4)	1.970(6)	V(5)-O(35)	1.927(5)
Sb(1)-O(3)	2.044(5)	V(5)-O(28)	1.942(5)
Sb(1)-N(31)	2.507(11)	V(5)-O(3)	1.963(6)
Sb(2)-O(8)	1.957(6)	V(5)-O(16)	1.995(5)
Sb(2)-O(7)	1.985(5)	V(6)-O(40)	1.610(5)
Sb(2)-O(6)	1.993(5)	V(6)-O(41)	1.909(5)
Sb(3)-O(11)	1.863(13)	V(6)-O(26)	1.937(5)
Sb(3)-O(12)	1.930(13)	V(6)-O(11)	1.993(6)
Sb(3)-O(10)	2.033(10)	V(6)-O(21)	2.005(5)
Ge(1)-O(1)	1.66(2)	V(7)-O(33)	1.609(5)
Ge(1)-O(3)	1.676(7)	V(7)-O(23)	1.937(5)
Ge(1)-O(2)	1.801(8)	V(7)-O(22)	1.939(5)
Ge(1)-O(4)	1.823(8)	V(7)-O(31)	1.940(5)
Ge(2)-O(5)	1.66(2)	V(7)-O(19)	2.027(5)
Ge(2)-O(6)	1.727(14)	V(8)-O(25)	1.611(5)
Ge(2)-O(7)	1.795(15)	V(8)-O(23)	1.910(5)
Ge(2)-O(8)	1.850(16)	V(8)-O(31)	1.940(5)
Ge(3)-O(9)	1.614(10)	V(8)-O(2)	1.985(5)
Ge(3)-O(10)	1.766(8)	V(8)-O(15)	2.005(6)
Ge(3)-O(12)	1.810(9)	V(9)-O(46)	1.611(5)
Ge(3)-O(11)	1.837(9)	V(9)-O(42)	1.933(5)
Ge(4)-O(17)	1.729(6)	V(9)-O(24)	1.945(5)
Ge(4)-O(16)	1.740(5)	V(9)-O(35)	1.949(5)
Ge(4)-O(18)	1.743(5)	V(9)-O(18)	2.024(5)
Ge(4)-O(8)	1.745(6)	V(10)-O(38)	1.617(5)
Ge(5)-O(20)	1.653(6)	V(10)-O(22)	1.930(5)
Ge(5)-O(19)	1.767(5)	V(10)-O(29)	1.936(5)
Ge(5)-O(21)	1.780(5)	V(10)-O(43)	1.955(5)
Ge(5)-O(12)	1.789(6)	V(10)-O(6)	1.984(6)
Ge(6)-O(14)	1.703(6)	V(11)-O(45)	1.598(5)

Ge(6)-O(15)	1.747(5)	V(11)-O(31)	1.938(5)
Ge(6)-O(13)	1.748(5)	V(11)-O(26)	1.943(5)
Ge(6)-O(4)	1.751(6)	V(11)-O(15)	1.989(5)
Ge(6)-Ge(1)	2.938(5)	V(11)-O(21)	1.995(5)
V(1)-O(47)	1.615(5)	V(12)-O(39)	1.609(5)
V(1)-O(42)	1.916(5)	V(12)-O(41)	1.934(5)
V(1)-O(35)	1.935(5)	V(12)-O(42)	1.938(5)
V(1)-O(3)	1.967(5)	V(12)-O(26)	1.960(5)
V(1)-O(13)	2.005(5)	V(12)-O(13)	2.026(5)
V(2)-O(44)	1.621(5)	V(13)-O(48)	1.621(5)
V(2)-O(27)	1.914(5)	V(13)-O(24)	1.915(6)
V(2)-O(43)	1.915(5)	V(13)-O(27)	1.938(5)
V(2)-O(10)	1.977(5)	V(13)-O(7)	1.968(5)
V(2)-O(7)	1.985(6)	V(13)-O(18)	1.998(5)
V(3)-O(36)	1.606(5)	V(14)-O(30)	1.622(5)
V(3)-O(24)	1.924(5)	V(14)-O(29)	1.924(5)
V(3)-O(41)	1.942(5)	V(14)-O(23)	1.939(5)
V(3)-O(27)	1.959(5)	V(14)-O(28)	1.956(5)
V(3)-O(11)	2.020(5)	V(14)-O(2)	1.989(6)
V(4)-O(32)	1.610(5)	V(15)-O(34)	1.610(5)
V(4)-O(29)	1.910(5)	V(15)-O(22)	1.905(5)
V(4)-O(28)	1.945(5)	V(15)-O(43)	1.953(5)
V(4)-O(6)	1.961(5)	V(15)-O(10)	1.978(5)
V(4)-O(16)	2.005(5)	V(15)-O(19)	1.999(6)

Tab. S 6: Bond lengths [Å] and angles [°] for the Ni complexes in compound **1**.

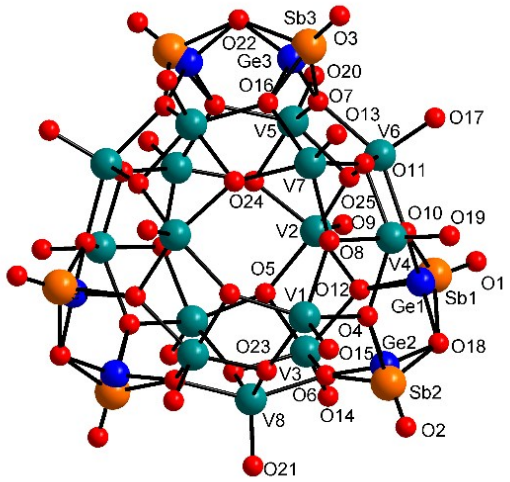
Ni(1)-N(6)	2.111(7)	Ni(1)-N(2)	2.138(7)
Ni(1)-N(5)	2.124(8)	Ni(1)-N(4)	2.141(7)
Ni(1)-N(1)	2.126(8)	Ni(1)-N(3)	2.156(8)
N(6)-Ni(1)-N(1)	92.6(3)	N(1)-Ni(1)-N(4)	171.3(3)
N(5)-Ni(1)-N(1)	93.7(3)	N(2)-Ni(1)-N(4)	93.2(3)
N(6)-Ni(1)-N(2)	90.4(3)	N(6)-Ni(1)-N(3)	173.1(3)
N(5)-Ni(1)-N(2)	170.4(3)	N(5)-Ni(1)-N(3)	94.5(4)
N(1)-Ni(1)-N(2)	81.1(3)	N(1)-Ni(1)-N(3)	93.4(3)
N(6)-Ni(1)-N(4)	93.9(3)	N(2)-Ni(1)-N(3)	93.9(3)
N(5)-Ni(1)-N(4)	92.9(3)	N(4)-Ni(1)-N(3)	80.4(3)
Ni(2)-N(12)	2.117(7)	Ni(2)-N(15)	2.127(7)
Ni(2)-N(14)	2.117(7)	Ni(2)-N(16)	2.139(8)
Ni(2)-N(13)	2.119(7)	Ni(2)-N(11)	2.146(7)
N(12)-Ni(2)-N(14)	93.2(3)	N(13)-Ni(2)-N(16)	172.8(3)
N(12)-Ni(2)-N(13)	91.6(3)	N(15)-Ni(2)-N(16)	81.0(3)
N(14)-Ni(2)-N(13)	82.2(3)	N(12)-Ni(2)-N(11)	81.4(3)
N(12)-Ni(2)-N(15)	172.7(3)	N(14)-Ni(2)-N(11)	172.3(3)
N(14)-Ni(2)-N(15)	92.4(3)	N(13)-Ni(2)-N(11)	92.5(3)
N(13)-Ni(2)-N(15)	93.7(3)	N(15)-Ni(2)-N(11)	93.4(3)
N(12)-Ni(2)-N(16)	94.2(3)	N(16)-Ni(2)-N(11)	92.7(3)
N(14)-Ni(2)-N(16)	93.1(3)		
Ni(3)-N(25)	2.109(7)	Ni(3)-N(22)	2.126(7)
Ni(3)-N(24)	2.110(7)	Ni(3)-N(26)	2.127(7)
Ni(3)-N(23)	2.120(7)	Ni(3)-N(21)	2.139(8)
N(25)-Ni(3)-N(24)	92.5(3)	N(23)-Ni(3)-N(26)	173.5(3)
N(25)-Ni(3)-N(23)	91.6(3)	N(22)-Ni(3)-N(26)	93.7(3)
N(24)-Ni(3)-N(23)	82.7(3)	N(25)-Ni(3)-N(21)	95.8(3)
N(25)-Ni(3)-N(22)	175.0(3)	N(24)-Ni(3)-N(21)	169.9(3)
N(24)-Ni(3)-N(22)	90.5(3)	N(23)-Ni(3)-N(21)	91.3(3)
N(23)-Ni(3)-N(22)	92.7(3)	N(22)-Ni(3)-N(21)	81.6(3)
N(25)-Ni(3)-N(26)	82.0(3)	N(26)-Ni(3)-N(21)	90.8(3)
N(24)-Ni(3)-N(26)	96.1(3)		

Tab. S 7: Geometric parameters for the proposed hydrogen bonds for compound **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(20)#1	0.91	2.62	3.318(10)	134.0
C(2)-H(2D)...O(36)#2	0.99	2.64	3.432(15)	136.7
N(2)-H(2A)...O(24)#2	0.91	2.37	3.247(10)	161.5
N(2)-H(2B)...O(46)#2	0.91	2.60	3.126(9)	117.9
N(3)-H(3A)...O(5)#3	0.91	2.28	3.19(3)	175.5
N(3)-H(3B)...O(33)#1	0.91	2.20	3.013(10)	148.0
C(3)-H(3C)...O(25)#1	0.99	2.50	3.418(13)	154.0
N(4)-H(4A)...O(42)#2	0.91	2.32	3.100(9)	143.8
N(4)-H(4A)...O(46)#2	0.91	2.52	3.296(9)	143.2
N(4)-H(4B)...O(39)#2	0.91	2.38	3.109(8)	137.1
N(5)-H(5B)...O(38)#3	0.91	2.22	3.030(10)	147.5
C(5)-H(5C)...O(39)#2	0.99	2.60	3.410(12)	139.1
C(5)-H(5D)...O(34)#3	0.99	2.52	3.477(12)	162.5
N(6)-H(6A)...O(39)#2	0.91	2.63	3.330(9)	134.8
N(6)-H(6A)...O(41)#2	0.91	2.31	3.148(9)	152.9
N(6)-H(6B)...O(36)#2	0.91	2.52	3.188(10)	130.1
N(11)-H(11A)...O(30)	0.91	2.44	3.110(8)	130.9
N(11)-H(11B)...O(29)	0.91	2.29	3.125(8)	151.5
N(11)-H(11B)...O(38)	0.91	2.63	3.362(9)	137.8
C(12)-H(12D)...O(47)#4	0.99	2.41	3.392(13)	170.6
N(12)-H(12A)...O(39)#4	0.91	2.41	3.176(10)	141.5
N(13)-H(13A)...O(38)	0.91	2.29	3.019(9)	136.4
N(13)-H(13B)...O(22)	0.91	2.26	3.071(8)	147.6
N(13)-H(13B)...O(33)	0.91	2.64	3.385(9)	139.8
C(14)-H(14D)...O(48)#5	0.99	2.49	3.444(11)	161.4
N(14)-H(14A)...O(46)#5	0.91	2.31	3.115(9)	147.0
N(15)-H(15A)...O(33)	0.91	2.32	3.079(9)	141.1
N(15)-H(15B)...O(23)	0.91	2.37	3.129(9)	140.7
N(15)-H(15B)...O(30)	0.91	2.60	3.401(9)	147.9
N(21)-H(21A)...O(48)#6	0.91	2.37	3.186(9)	148.8
N(22)-H(22A)...O(30)	0.91	2.22	3.122(8)	169.7
N(22)-H(22B)...O(40)#2	0.91	2.28	3.137(9)	157.5
N(23)-H(23A)...O(48)#6	0.91	2.22	3.047(8)	150.7
N(23)-H(23B)...O(40)#2	0.91	2.18	3.036(9)	155.5
C(23)-H(23C)...O(21)#2	0.99	2.65	3.567(12)	154.1
C(23)-H(23D)...O(44)#6	0.99	2.39	3.371(13)	169.5
C(24)-H(24C)...O(37)	0.99	2.64	3.383(12)	132.0
N(24)-H(24A)...O(28)	0.91	2.38	3.140(8)	141.6
N(25)-H(25A)...O(27)#6	0.91	2.65	3.144(8)	114.7
N(25)-H(25A)...O(48)#6	0.91	2.58	3.224(9)	128.4
N(25)-H(25B)...O(44)#6	0.91	2.55	3.446(10)	167.2
C(25)-H(25C)...O(9)#6	0.99	2.62	3.257(14)	122.3
C(25)-H(25D)...O(32)	0.99	2.66	3.374(11)	129.3
N(26)-H(26A)...O(32)	0.91	2.21	2.995(9)	144.2
N(31)-H(31A)...O(25)	0.91	2.28	3.127(12)	155.5
C(31)-H(31C)...O(30)	0.99	2.51	3.489(17)	171.5

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y-1/2,-z+1 #2 -x+1,y-1/2,-z #3 -x+2,y-1/2,-z+1 #4 x+1,y,z+1 #5 x,y,z+1 #6 -x+2,y-1/2,-z

Tab. S 8: Bond lengths [Å] for the anion in compound **2**.



Sb(1)-O(12)	1.946(4)	V(3)-O(23)	1.947(4)
Sb(1)-O(18)	1.976(4)	V(3)-O(12)	1.977(4)
Sb(1)-O(10)	1.990(5)	V(3)-O(6)	1.979(4)
Sb(2)-O(4)	1.948(5)	V(4)-O(19)	1.629(4)
Sb(2)-O(18)	1.977(5)	V(4)-O(8)	1.910(4)
Sb(2)-O(6)	1.979(4)	V(4)-O(11)	1.937(4)
Sb(3)-O(7)	1.920(5)	V(4)-O(10)	1.974(4)
Sb(3)-O(22)	1.970(3)	V(4)-O(4)	1.991(4)
Sb(3)-O(16)	2.053(5)	V(5)-O(20)	1.611(5)
Ge(1)-O(1)	1.721(16)	V(5)-O(24)	1.919(4)
Ge(1)-O(18)	1.737(6)	V(5)-O(25)	1.939(4)
Ge(1)-O(10)	1.769(7)	V(5)-O(7)	1.982(5)
Ge(1)-O(12)	1.770(6)	V(5)-O(16)#1	1.982(5)
Ge(1)-Ge(2)	2.848(4)	V(6)-O(17)	1.614(4)
Ge(2)-O(2)	1.716(7)	V(6)-O(25)	1.919(4)
Ge(2)-O(18)	1.721(5)	V(6)-O(11)	1.920(5)
Ge(2)-O(4)	1.759(5)	V(6)-O(10)	1.989(4)
Ge(2)-O(6)	1.769(4)	V(6)-O(7)	1.989(4)
Ge(3)-O(3)	1.686(8)	V(7)-O(13)	1.616(4)
Ge(3)-O(16)	1.702(5)	V(7)-O(24)#1	1.920(4)
Ge(3)-O(22)	1.758(4)	V(7)-O(8)	1.934(4)
Ge(3)-O(7)	1.820(5)	V(7)-O(11)	1.956(4)
Ge(3)-Ge(3)#1	2.924(4)	V(7)-O(16)	2.011(4)
V(1)-O(15)	1.620(4)	V(8)-O(21)	1.609(6)
V(1)-O(8)#1	1.935(4)	V(8)-O(23)#1	1.921(4)
V(1)-O(5)	1.944(4)	V(8)-O(23)	1.921(4)
V(1)-O(23)	1.960(4)	V(8)-O(6)#1	1.991(4)
V(1)-O(4)#1	1.997(4)	V(8)-O(6)	1.991(4)
V(2)-O(9)	1.612(5)	O(4)-V(1)#1	1.997(4)
V(2)-O(24)	1.930(4)	O(8)-V(1)#1	1.935(4)
V(2)-O(5)	1.936(4)	O(16)-V(5)#1	1.982(4)
V(2)-O(25)	1.945(4)	O(22)-Ge(3)#1	1.758(4)
V(2)-O(12)	2.009(4)	O(22)-Sb(3)#1	1.970(3)
V(3)-O(14)	1.619(4)	O(24)-V(7)#1	1.920(4)
V(3)-O(5)	1.916(4)		

Symmetry transformations used to generate equivalent atoms: #1 -x+2,y,-z+2 #2 -x+1,y,-z+1

Tab. S 9: Bond lengths [Å] and angles [°] for the Ni complexes in compound **2**.

Ni(1)-N(5)	2.110(6)	Ni(2)-N(11)#2	2.129(6)
Ni(1)-N(2)	2.116(6)	Ni(2)-N(11)	2.129(6)
Ni(1)-N(6)	2.134(6)	Ni(2)-N(13)	2.133(6)
Ni(1)-N(4)	2.135(5)	Ni(2)-N(13)#2	2.133(6)
Ni(1)-N(3)	2.142(6)	Ni(2)-N(12)#2	2.134(6)
Ni(1)-N(1)	2.147(5)	Ni(2)-N(12)	2.134(6)
N(5)-Ni(1)-N(2)	170.8(2)	N(11)#2-Ni(2)-N(11)	173.7(3)
N(5)-Ni(1)-N(6)	82.7(3)	N(11)#2-Ni(2)-N(13)	91.5(2)
N(2)-Ni(1)-N(6)	91.2(3)	N(11)-Ni(2)-N(13)	93.2(3)
N(5)-Ni(1)-N(4)	95.0(2)	N(11)#2-Ni(2)-N(13)#2	93.2(2)
N(2)-Ni(1)-N(4)	92.0(2)	N(11)-Ni(2)-N(13)#2	91.5(2)
N(6)-Ni(1)-N(4)	91.5(2)	N(13)-Ni(2)-N(13)#2	81.0(3)
N(5)-Ni(1)-N(3)	92.3(3)	N(11)#2-Ni(2)-N(12)#2	81.3(3)
N(2)-Ni(1)-N(3)	94.6(2)	N(11)-Ni(2)-N(12)#2	94.2(2)
N(6)-Ni(1)-N(3)	170.9(2)	N(13)-Ni(2)-N(12)#2	94.6(2)
N(4)-Ni(1)-N(3)	81.3(2)	N(13)#2-Ni(2)-N(12)#2	173.0(2)
N(5)-Ni(1)-N(1)	92.2(2)	N(11)#2-Ni(2)-N(12)	94.2(2)
N(2)-Ni(1)-N(1)	81.7(2)	N(11)-Ni(2)-N(12)	81.3(3)
N(6)-Ni(1)-N(1)	97.2(2)	N(13)-Ni(2)-N(12)	173.0(2)
N(4)-Ni(1)-N(1)	169.3(2)	N(13)#2-Ni(2)-N(12)	94.6(2)
N(3)-Ni(1)-N(1)	90.6(2)	N(12)#2-Ni(2)-N(12)	

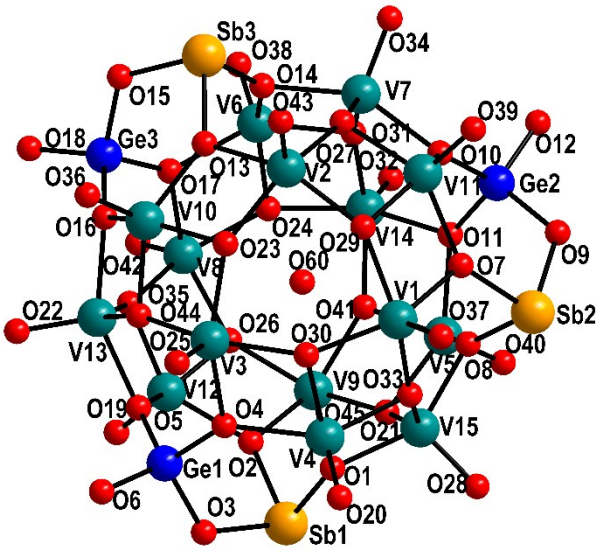
Symmetry transformations used to generate equivalent atoms: #1 -x+2,y,-z+2 #2 -x+1,y,-z+1

Tab. S 10: Geometric parameters of the proposed hydrogen bonds for compound **2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1C)...O(9)#3	0.91	2.40	3.125(7)	136.9
C(1)-H(1B)...O(1)#3	0.99	2.64	3.218(18)	117.2
C(2)-H(2A)...O(25)#3	0.99	2.57	3.442(9)	146.5
C(2)-H(2B)...O(1)#3	0.99	2.53	3.149(17)	120.5
N(2)-H(2C)...O(17)#4	0.91	2.07	2.958(7)	166.0
N(3)-H(3C)...O(17)#4	0.91	2.45	3.217(7)	142.6
C(4)-H(4A)...O(17)#4	0.99	2.62	3.449(8)	141.1
C(4)-H(4B)...O(2)#1	0.99	2.48	3.242(10)	133.5
N(4)-H(4C)...O(23)	0.91	2.44	3.222(6)	144.0
N(5)-H(5C)...O(21)	0.91	2.10	2.947(7)	153.5
N(6)-H(6C)...O(20)#3	0.91	2.22	3.062(9)	152.9
N(6)-H(6D)...O(14)	0.91	2.27	3.101(7)	151.1
N(11)-H(11C)...O(15)	0.91	2.22	3.092(7)	160.4
C(11)-H(11B)...O(9)#2	0.99	2.56	3.435(9)	146.8
N(12)-H(12C)...O(5)#2	0.91	2.24	3.109(7)	159.3
N(12)-H(12D)...O(15)#2	0.91	2.55	3.101(8)	119.7
N(13)-H(13C)...O(13)#1	0.91	2.52	3.323(8)	148.0
N(13)-H(13C)...O(24)	0.91	2.41	3.096(7)	132.5
N(13)-H(13D)...O(9)	0.91	2.20	3.017(7)	149.6

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,-z+2 #2 -x+1,y,-z+1 #3 -x+3/2,y-1/2,-z+1; #4 x-1/2,y-1/2,z.

Tab. S 11: Selected bond lengths [Å] for the anion in compound **3**.



Sb(1)-O(1)	1.966(8)	Sb(2)-O(8)	1.984(8)
Sb(1)-O(3)	1.986(8)	Sb(3)-O(14)	1.935(7)
Sb(1)-O(2)	1.990(7)	Sb(3)-O(13)	1.955(8)
Sb(2)-O(7)	1.963(7)	Sb(3)-O(15)	1.971(9)
Sb(2)-O(9)	1.978(8)		
Ge(1)-O(6)	1.657(9)	Ge(2)-O(10)	1.770(8)
Ge(1)-O(5)	1.747(8)	Ge(2)-O(9)	1.771(8)
Ge(1)-O(4)	1.748(8)	Ge(3)-O(18)	1.671(10)
Ge(1)-O(3)	1.753(8)	Ge(3)-O(16)	1.731(8)
Ge(2)-O(12)	1.635(9)	Ge(3)-O(17)	1.732(8)
Ge(2)-O(11)	1.755(9)	Ge(3)-O(15)	1.750(9)
V(1)-O(37)	1.615(8)	V(8)-O(35)	1.949(8)
V(1)-O(30)	1.948(8)	V(8)-O(17)	2.006(9)
V(1)-O(33)	1.955(8)	V(8)-V(12)	2.853(3)
V(1)-O(29)	1.958(8)	V(9)-O(45)	1.607(9)
V(1)-O(7)	2.004(7)	V(9)-O(26)	1.938(8)
V(2)-O(43)	1.604(8)	V(9)-O(41)	1.942(8)
V(2)-O(29)	1.927(8)	V(9)-O(21)	1.942(8)
V(2)-O(23)	1.933(8)	V(9)-O(2)	1.997(7)
V(2)-O(27)	1.956(7)	V(10)-O(36)	1.619(8)
V(2)-O(13)	2.009(8)	V(10)-O(23)	1.898(8)
V(3)-O(25)	1.606(8)	V(10)-O(44)	1.922(8)
V(3)-O(30)	1.926(8)	V(10)-O(13)	1.969(8)
V(3)-O(23)	1.930(8)	V(10)-O(16)	1.998(8)
V(3)-O(44)	1.967(8)	V(11)-O(39)	1.606(9)
V(3)-O(4)	2.005(8)	V(11)-O(29)	1.923(7)
V(4)-O(20)	1.596(8)	V(11)-O(27)	1.943(8)
V(4)-O(30)	1.913(8)	V(11)-O(7)	1.971(8)
V(4)-O(33)	1.947(7)	V(11)-O(10)	2.000(7)
V(4)-O(1)	1.975(8)	V(12)-O(19)	1.621(9)
V(4)-O(4)	2.016(8)	V(12)-O(26)	1.912(8)
V(5)-O(40)	1.605(8)	V(12)-O(35)	1.952(8)
V(5)-O(41)	1.910(7)	V(12)-O(2)	1.956(7)
V(5)-O(21)	1.952(8)	V(12)-O(5)	2.024(7)
V(5)-O(8)	1.954(8)	V(13)-O(22)	1.605(9)

V(5)-O(11)	2.015(8)	V(13)-O(44)	1.912(8)
V(6)-O(38)	1.609(8)	V(13)-O(35)	1.916(8)
V(6)-O(24)	1.920(8)	V(13)-O(5)	1.988(8)
V(6)-O(31)	1.952(8)	V(13)-O(16)	2.015(8)
V(6)-O(14)	1.977(8)	V(14)-O(32)	1.607(7)
V(6)-O(17)	2.005(8)	V(14)-O(24)	1.932(8)
V(7)-O(34)	1.597(9)	V(14)-O(41)	1.950(8)
V(7)-O(31)	1.924(8)	V(14)-O(31)	1.951(8)
V(7)-O(27)	1.934(8)	V(14)-O(11)	2.027(8)
V(7)-O(14)	1.980(8)	V(15)-O(28)	1.609(7)
V(7)-O(10)	1.982(8)	V(15)-O(21)	1.926(8)
V(7)-V(11)	3.038(2)	V(15)-O(33)	1.933(7)
V(8)-O(42)	1.606(8)	V(15)-O(1)	1.960(8)
V(8)-O(24)	1.922(8)	V(15)-O(8)	1.960(8)
V(8)-O(26)	1.937(8)		

Tab. S 12: Bond lengths [Å] and angles of the Ni complexes [°] for compound **3**.

Ni(1)-N(22)	2.104(12)	Ni(1)-N(21)	2.129(12)
Ni(1)-N(11)	2.111(10)	Ni(1)-N(12)	2.130(10)
Ni(1)-N(2)	2.120(10)	Ni(1)-N(1)	2.138(13)
N(22)-Ni(1)-N(11)	172.4(5)	N(21)-Ni(1)-N(12)	94.2(4)
N(22)-Ni(1)-N(2)	93.7(5)	N(22)-Ni(1)-N(1)	92.3(6)
N(11)-Ni(1)-N(2)	92.8(5)	N(11)-Ni(1)-N(1)	92.5(6)
N(22)-Ni(1)-N(21)	81.9(5)	N(2)-Ni(1)-N(1)	81.7(5)
N(11)-Ni(1)-N(21)	94.0(5)	N(21)-Ni(1)-N(1)	170.8(5)
N(2)-Ni(1)-N(21)	91.6(5)	N(12)-Ni(1)-N(1)	93.0(5)
N(22)-Ni(1)-N(12)	91.5(4)	C(1')-N(1)-Ni(1)	109.3(16)
N(11)-Ni(1)-N(12)	82.4(4)	C(1)-N(1)-Ni(1)	103.7(12)
N(2)-Ni(1)-N(12)	172.7(5)		
Ni(2)-N(31)	2.01(2)	Ni(2)-N(32)	2.130(12)
Ni(2)-N(52')	2.07(4)	Ni(2)-N(51')	2.14(3)
Ni(2)-N(42)	2.120(16)	Ni(2)-N(52)	2.164(16)
Ni(2)-N(41)	2.123(11)	Ni(2)-N(51)	2.167(18)
N(31)-Ni(2)-N(52')	64.8(12)	N(42)-Ni(2)-N(51')	113.2(15)
N(31)-Ni(2)-N(42)	175.3(7)	N(41)-Ni(2)-N(51')	164.6(14)
N(52')-Ni(2)-N(42)	116.3(11)	N(32)-Ni(2)-N(51')	91.3(12)
N(31)-Ni(2)-N(41)	94.9(7)	N(31)-Ni(2)-N(52)	92.8(8)
N(52')-Ni(2)-N(41)	86.0(11)	N(42)-Ni(2)-N(52)	89.3(6)
N(42)-Ni(2)-N(41)	80.7(5)	N(41)-Ni(2)-N(52)	95.0(6)
N(31)-Ni(2)-N(32)	85.1(7)	N(32)-Ni(2)-N(52)	170.4(5)
N(52')-Ni(2)-N(32)	149.8(11)	N(31)-Ni(2)-N(51)	98.4(8)
N(42)-Ni(2)-N(32)	93.5(5)	N(42)-Ni(2)-N(51)	86.2(6)
N(41)-Ni(2)-N(32)	94.5(5)	N(41)-Ni(2)-N(51)	165.9(6)
N(31)-Ni(2)-N(51')	71.4(15)	N(32)-Ni(2)-N(51)	91.4(6)
N(52')-Ni(2)-N(51')	81.9(15)	N(52)-Ni(2)-N(51)	79.7(6)
Ni(3)-N(61)	2.101(12)	Ni(3)-N(71)	2.136(13)
Ni(3)-N(72)	2.109(13)	Ni(3)-N(62)	2.136(10)
Ni(3)-N(81)	2.123(10)	Ni(3)-N(82)	2.150(10)
N(61)-Ni(3)-N(72)	92.0(6)	N(81)-Ni(3)-N(62)	90.9(4)
N(61)-Ni(3)-N(81)	90.5(4)	N(71)-Ni(3)-N(62)	93.4(5)
N(72)-Ni(3)-N(81)	176.8(6)	N(61)-Ni(3)-N(82)	95.7(4)
N(61)-Ni(3)-N(71)	171.9(6)	N(72)-Ni(3)-N(82)	96.1(5)
N(72)-Ni(3)-N(71)	81.2(7)	N(81)-Ni(3)-N(82)	81.6(4)
N(81)-Ni(3)-N(71)	96.5(5)	N(71)-Ni(3)-N(82)	89.4(5)
N(61)-Ni(3)-N(62)	82.4(4)	N(62)-Ni(3)-N(82)	172.2(4)
N(72)-Ni(3)-N(62)	91.4(5)		

Tab. S 13: Geometric parameters of the proposed hydrogen bonds for compound **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1F)...O(56)#1	0.91	2.63	3.44(2)	148.7
N(1)-H(1H)...O(51)	0.91	2.41	3.28(3)	162.4
C(2)-H(2A)...O(28)	0.99	2.61	3.465(17)	144.1
N(2)-H(2F)...O(29)#2	0.91	2.30	3.181(13)	161.8
N(11)-H(11C)...O(43)#2	0.91	2.35	3.085(13)	138.0
N(11)-H(11D)...O(23)#2	0.91	2.34	3.140(12)	145.9
N(11)-H(11D)...O(25)#2	0.91	2.64	3.427(15)	144.6
C(12)-H(12B)...O(38)#1	0.99	2.38	3.247(15)	145.4
N(12)-H(12C)...O(32)#1	0.91	2.27	3.118(14)	155.1
N(12)-H(12D)...O(54)#3	0.91	2.41	3.290(18)	162.1
N(21)-H(21D)...O(30)#2	0.91	2.28	3.167(14)	165.0
C(21)-H(21A)...O(37)#2	0.99	2.58	3.374(16)	137.7
C(22)-H(22A)...O(32)#1	0.99	2.49	3.407(16)	154.8
N(22)-H(22C)...O(45)	0.91	2.16	3.022(14)	158.1
N(22)-H(22D)...O(12)#1	0.91	2.47	3.147(14)	131.3
N(22)-H(22D)...O(56)#1	0.91	2.28	3.16(2)	161.6
N(31)-H(31E)...O(6)#4	0.91	2.38	3.23(2)	155.6
N(31)-H(31E)...O(6)#4	0.91	2.38	3.23(2)	155.6
N(31)-H(31G)...O(58)#4	0.91	2.58	3.40(3)	149.8
C(31')-H(31D)...O(6)#4	0.99	2.40	3.14(4)	130.9
N(32)-H(32E)...O(24)	0.91	2.34	3.139(13)	146.9
N(32)-H(32F)...O(32)	0.91	2.26	2.990(14)	136.6
N(41)-H(41D)...O(25)#4	0.91	2.29	3.162(16)	159.5
C(41)-H(41A)...O(20)#4	0.99	2.41	3.34(2)	156.2
C(42)-H(42A)...O(12)#1	0.99	2.61	3.57(3)	163.9
N(42)-H(42C)...O(41)	0.91	2.25	3.079(15)	151.2
N(42)-H(42D)...O(45)	0.91	2.30	3.013(13)	135.3
N(51)-H(51E)...O(26)	0.91	2.24	3.127(18)	166.1
N(52)-H(52F)...O(12)#1	0.91	2.44	3.28(2)	154.2
N(52')-H(52G)...O(58)#4	0.91	2.66	3.54(4)	164.4
N(52')-H(52H)...O(9)#1	0.91	2.12	2.99(4)	158.4
N(61)-H(61C)...O(39)#2	0.91	2.21	3.095(14)	164.7
C(61)-H(61B)...O(43)#2	0.99	2.39	3.358(17)	167.2
C(62)-H(62B)...O(34)#2	0.99	2.53	3.321(18)	136.5
N(62)-H(62C)...O(38)#6	0.91	2.59	3.418(15)	151.6
N(62)-H(62D)...O(18)#6	0.91	2.32	3.186(14)	159.0
N(71)-H(71E)...O(15)#6	0.91	2.39	3.226(14)	153.1
N(71)-H(71H)...O(19)#7	0.91	2.50	3.393(18)	166.6
N(71)-H(71E)...O(15)#6	0.91	2.39	3.226(14)	153.1
N(71)-H(71H)...O(19)#7	0.91	2.50	3.393(18)	166.6
C(72)-H(72A)...O(18)#6	0.99	2.66	3.57(3)	153.1
C(71')-H(71D)...O(18)#6	0.99	2.48	3.44(5)	164.9
N(72)-H(72E)...O(20)	0.91	2.02	2.897(14)	161.9
N(81)-H(81C)...O(38)#6	0.91	2.06	2.958(12)	168.9
N(81)-H(81D)...O(59)#3	0.91	2.56	3.44(3)	162.1
C(81)-H(81B)...O(19)#7	0.99	2.42	3.197(17)	134.4
N(82)-H(82C)...O(28)	0.91	2.56	3.234(14)	131.0
N(82)-H(82C)...O(33)	0.91	2.55	3.389(12)	153.6
N(82)-H(82D)...O(19)#7	0.91	2.50	3.188(15)	132.4

Symmetry transformations used to generate equivalent atoms: #1 -x+2,y+1/2,-z+1; #2-x+1,y+1/2,-z+1; #3 x,y,z-1; #4 x+1,y,z; #5 -x+2,y+1/2,-z+2; #6 x-1,y,z-1; #7 -x+1,y-1/2,-z+1.

Tab. S 14: Mixed occupancies of the heteroatom positions in **1** and **2**.

Compound		**Ge[%]**	**Sb [%]**
1	Ge(1):Sb(1)	20	80
1	Ge(2):Sb(2)	10	90
1	Ge(3):Sb(3)	70	30
2	Ge(1):Sb(1)	30	70
2	Ge(2):Sb(2)	65	35
2	Ge(3):Sb(3)	55	45

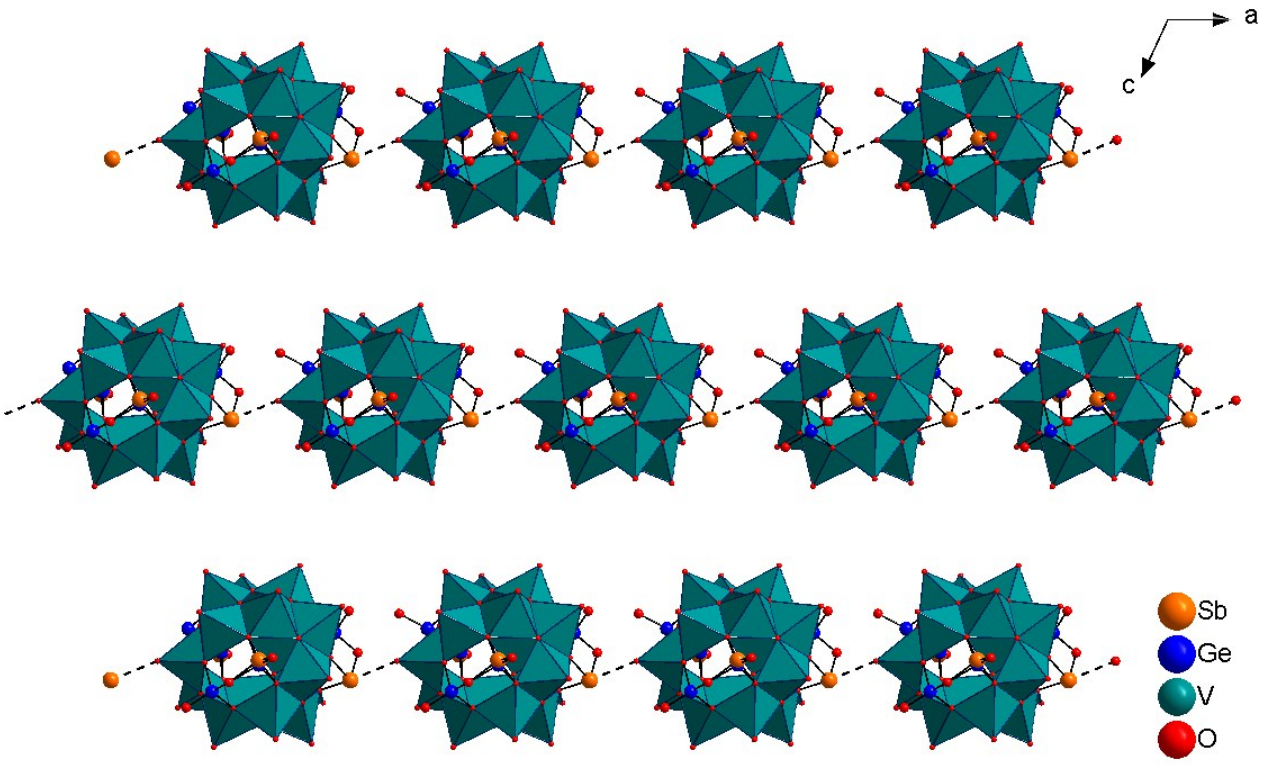


Fig. S 10: Chains of cluster anions generated by short Sb···O intercluster interactions (dashed lines) along [100].

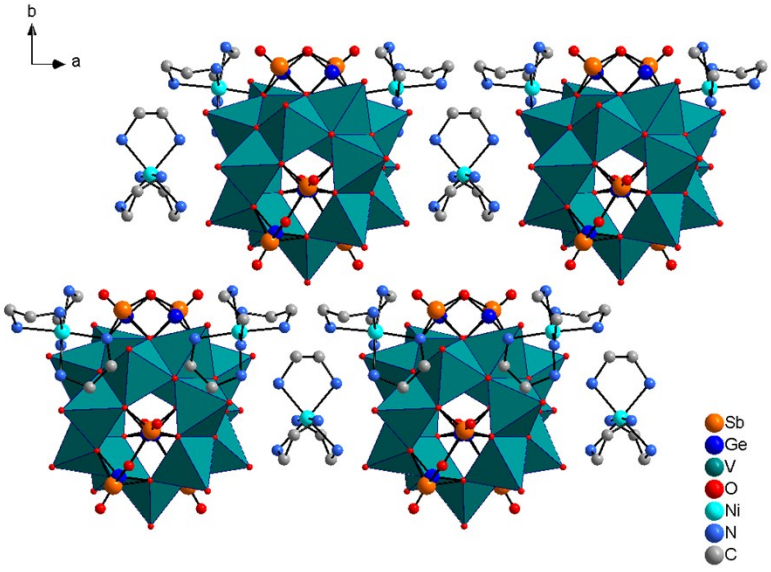


Fig. S 11: Alternating cations and the cluster anions in **2**. H-atoms have been omitted for clarity.

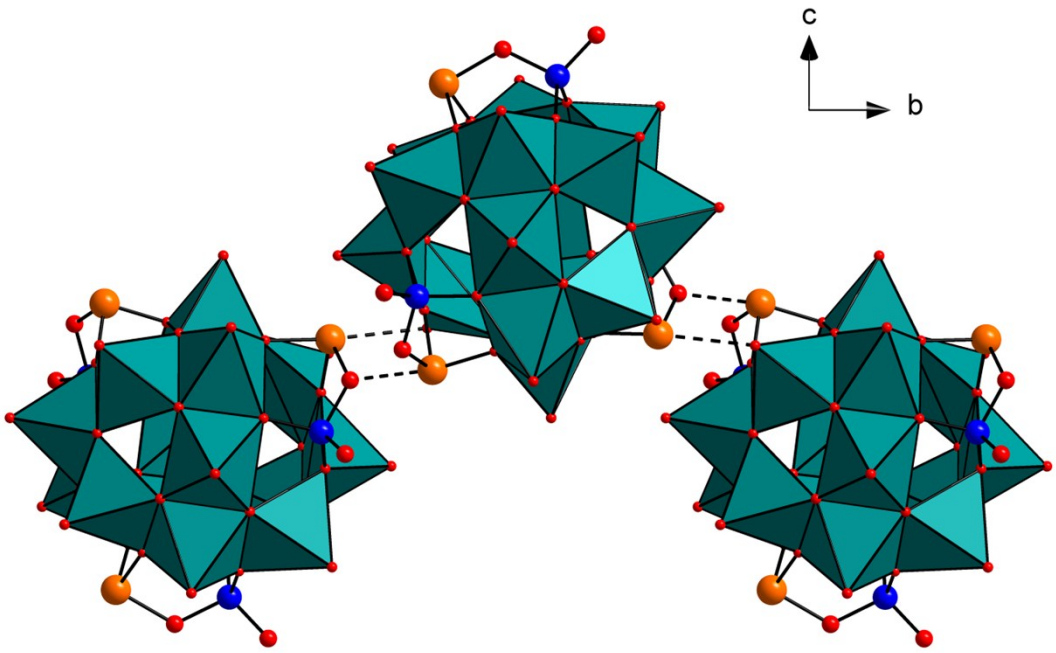


Fig. S 12: Intermolecular Sb···O contacts (dashed lines) between the anions in the structure of **3** generating a wavy chain along [010].

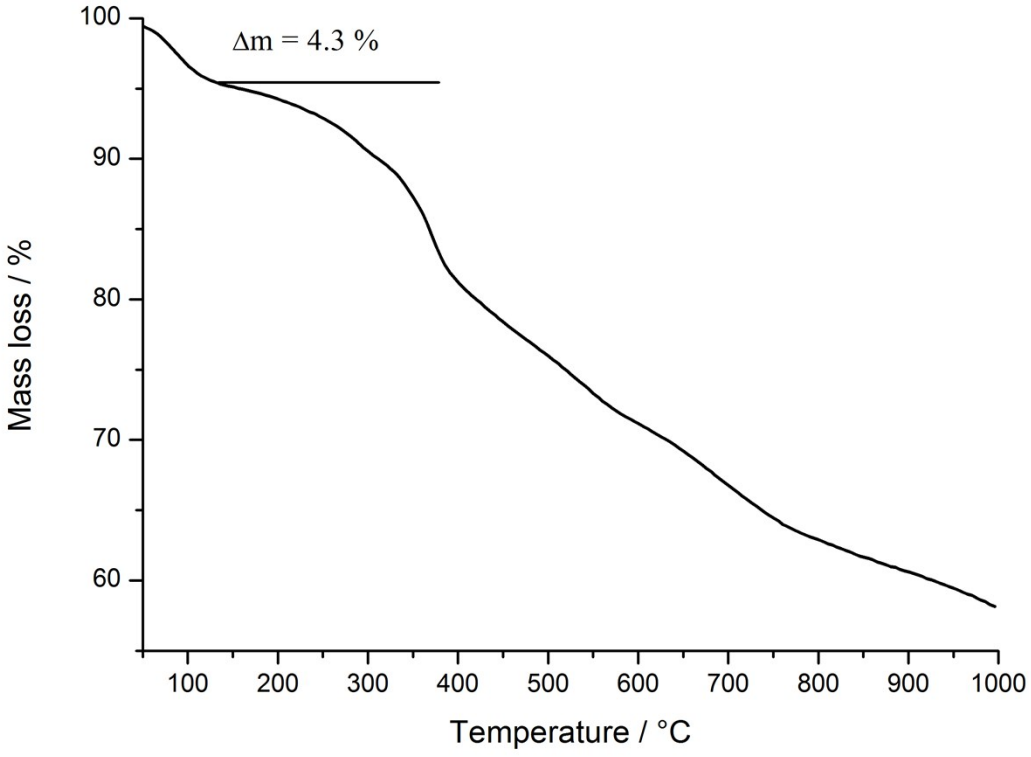


Fig. S 13: TG curve of compound **1**.

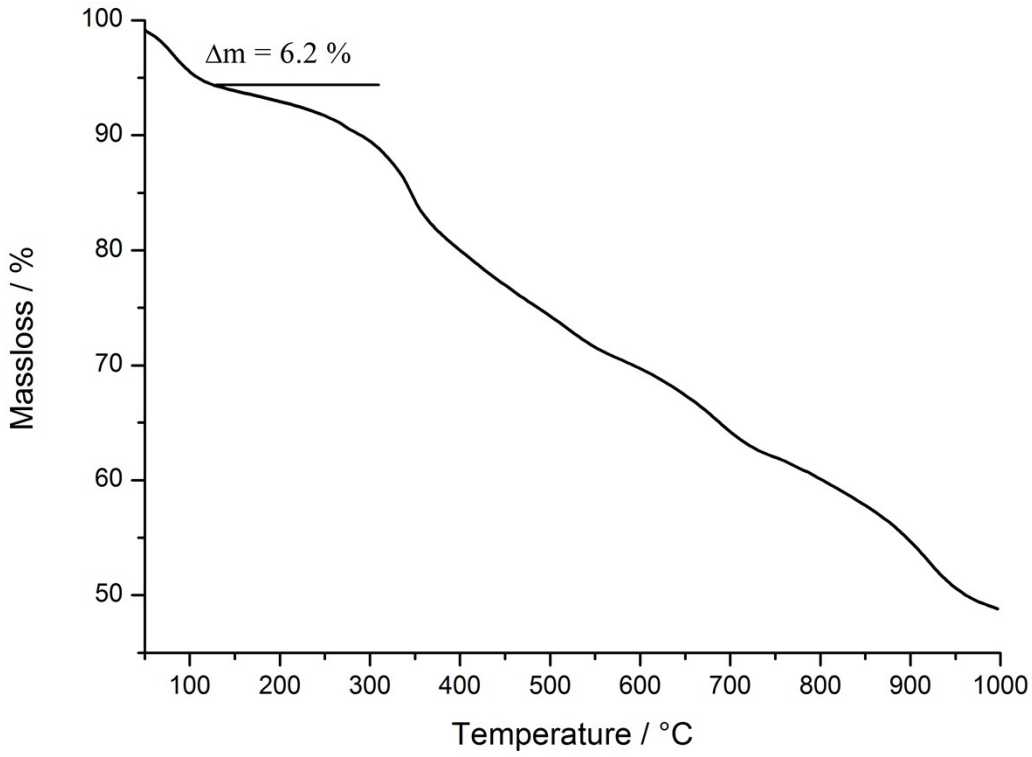


Fig. S14: TG curve of compound **2**.

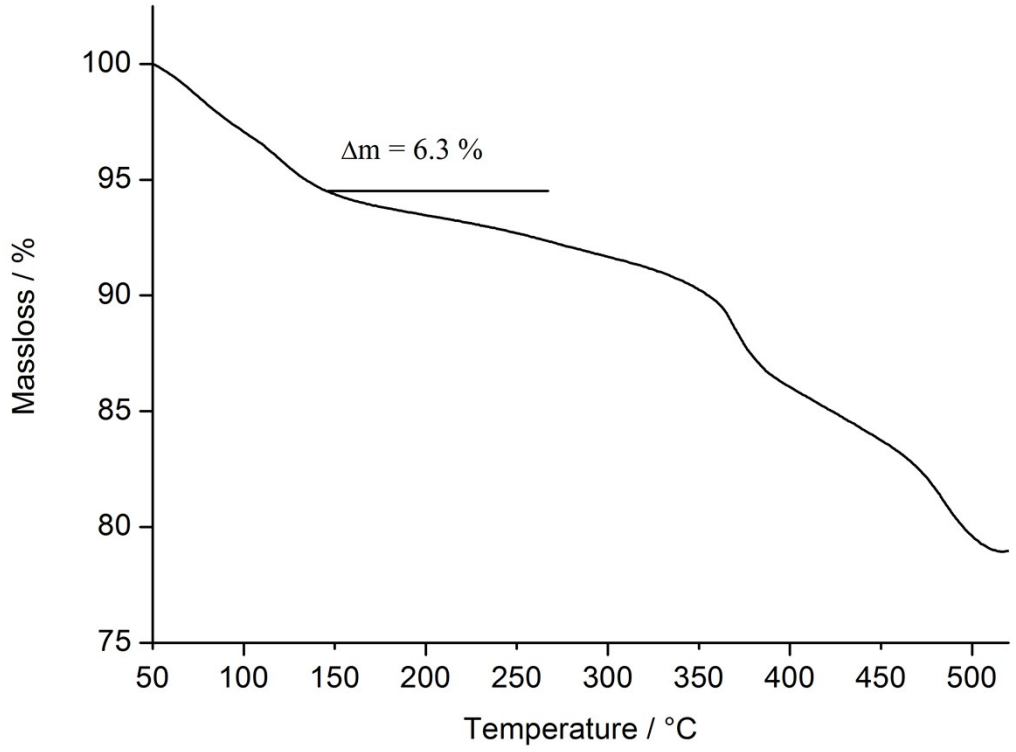


Fig. S15: TG curve of compound **3**.