Supplemental Material

$Nb_2S_4(CS_2NH_2)_4$ – A new precursor for NbS_2 and its transition metal inserted derivatives

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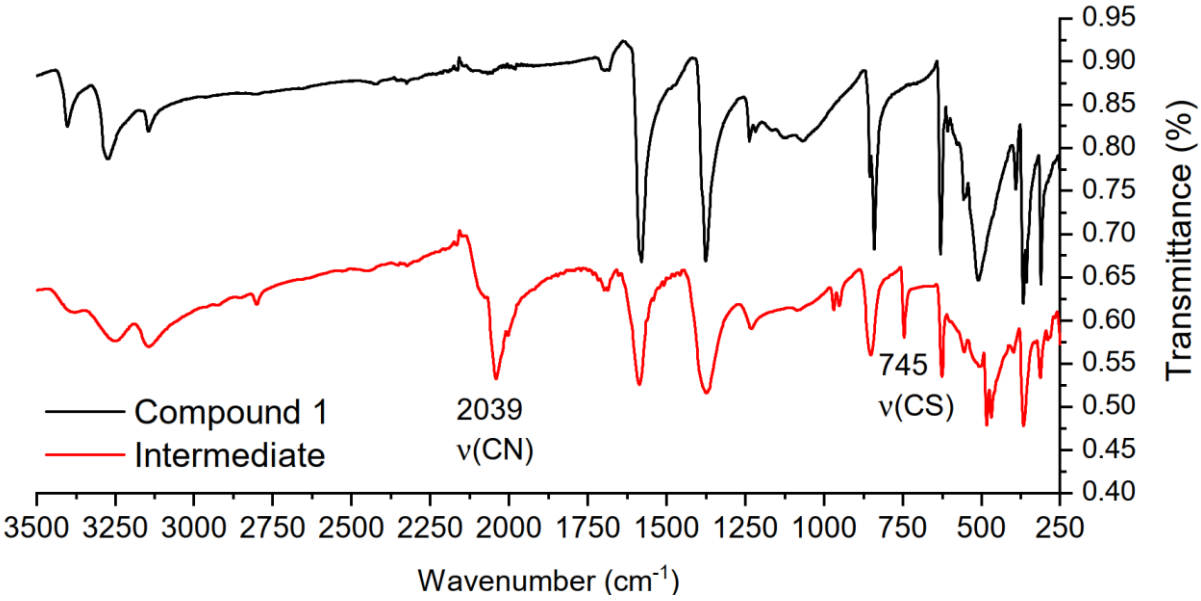

Figure S1: Comparison of the IR-spectra of **1** and the intermediate isolated directly after mixing the solutions of $NH_4CS_2NH_2$ and $[Nb_2S_4(NCS)_8]^{4-}$. Indicated are the two strongest bands of the NCS-ligand.

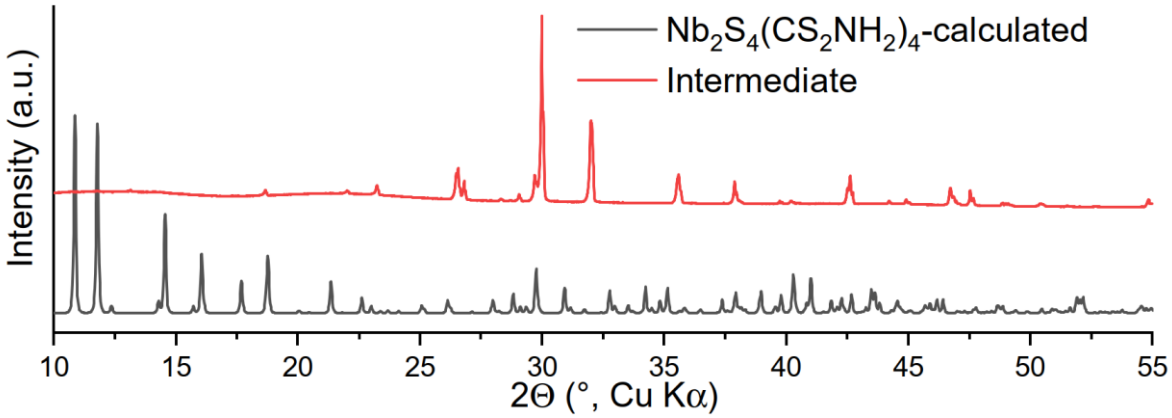

Figure S2: Comparison of the XRPD patterns for the intermediate in the preparation of **1** and the ansolvate of **1**.

Further discussion of the intermediate in the preparation of **1**:

The diffraction pattern in Figure S2 can be indexed with an orthorhombic unit cell of 1375 Å^3 volume. This corresponds to 60 atoms in the unit cell assuming 23 Å^3 per non H-atom like for **1**. It is likely that Z = 2. EDX spectroscopy yielded a ratio of Nb:K:S of 2:3:13. The incorporation of potassium makes a charged complex anion likely with some remaining thiocyanate ligands (c.f. IR spectrum in Figure S1) that create the net negative charge. The crystal structure could not be solved from XRPD data and single crystal growth of the soluble intermediate failed. Thus the structure remains unclear.

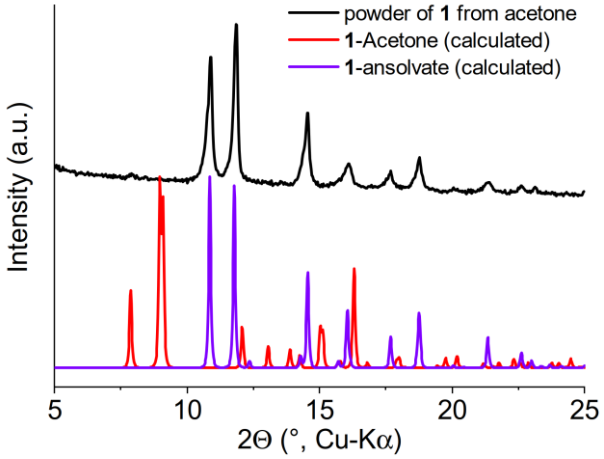

Figure S3: Comparison of the XRPD pattern obtained for **1** crystallized from acetone compared to the crystal structure of **1**-Acetone and the ansolvate.

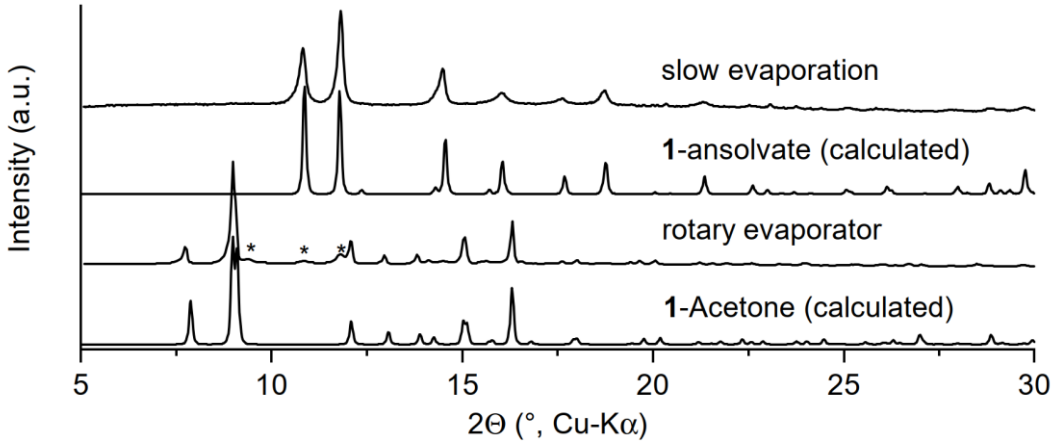

Figure S4: Comparison of XRPD patterns dry residues obtained after drying solution of $Nb_2S_4(CS_2NH_2)$ in acetone under different conditions. Calculated patterns are shown for comparison. Unidentified reflections are marked with an asterisk.

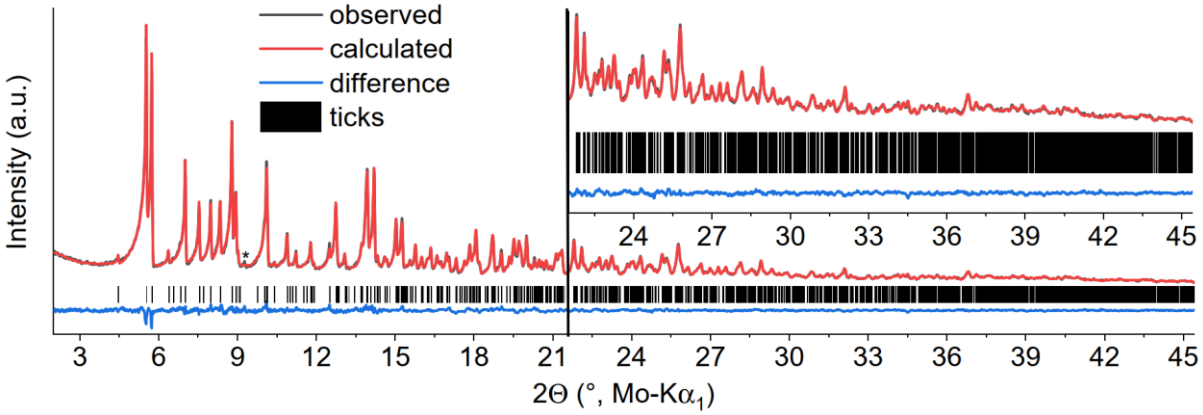

Figure S5: Difference plot of the final Rietveld refinement for $Co(CS_2NH_2)_3 \cdot H_2O$. The unindexed line is marked with an asterisk.

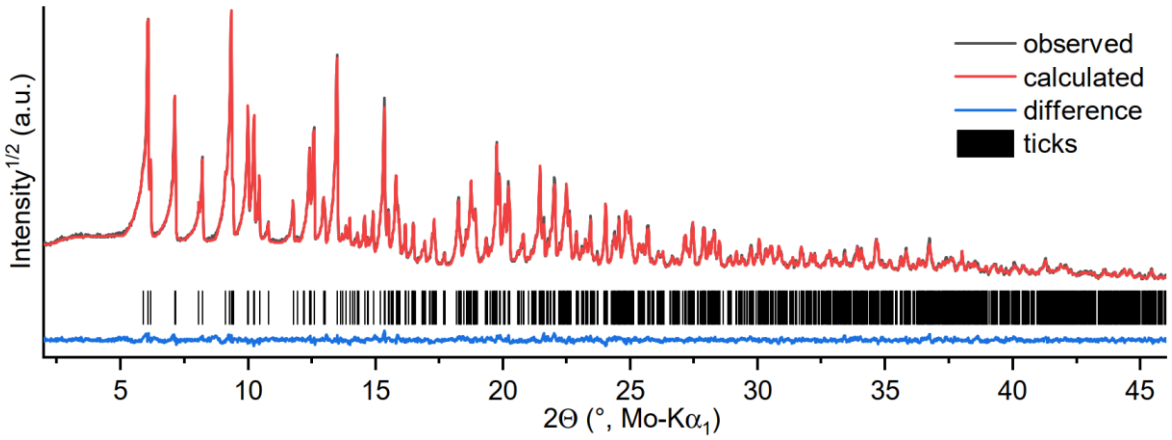

Figure S6: Difference plot of the final Rietveld refinement of the crystal structure of $Pd(CS_2NH_2)_2$.

Table S1 Details of the refinement for $Co(CS_2NH_2)_3 \cdot H_2O$ and $Pd(CS_2NH_2)_2$.

Formula	$C_3H_8Co_1N_3O_1S_6$	$C_2H_4N_2Pd_1S_4$
MW, g mol^{-1}	353.45	290.71
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	7.15513(14)	9.07466(13)
b, Å	14.6650(3)	10.06595(15)
c, Å	11.7192(2)	11.35377(16)
α, °	90	90
β, °	99.0641(19)	130.4697(8)
γ, °	90	90
V, Å^3	1214.34(5)	788.98(2)
T, K	295(2)	295(2)
Z	4	4
D_{calc}, g cm^{-3}	1.88912(7)	2.44770(7)
Θ_{max}, °	45.4	46.5
R_{Bragg}	1.53	1.41
R_{wp}	3.05	3.02
R_{exp}	3.25	2.33
GOF	0.94	1.29

Table S2. Selected crystal data and results of the structure refinements for compound **1** and **1-Acetone**.

Compound	**1**	**1-Acetone**
Sum formula	$C_4H_{8.8}N_4Nb_2O_{0.4}S_{12}$	$C_{16}H_{32}N_4Nb_2O_4S_{12}$
MW/g mol^{-1}	689.89	914.99
Crystal system	orthorhombic	triclinic
Space group	*Pbcn*	*P*-1
a / Å	10.9572(2)	7.4929(6)
b / Å	12.1617(3)	10.9104(8)
c / Å	15.0072(3)	12.6724(9)
α / °	90	115.449(5)
β / °	90	98.079(6)
γ / °	90	94.981(6)
V / Å^3	1999.83(7)	913.52(12)
T / K	100(2)	200(2)
Z	4	1
D_{calc}/g cm^{-3}	2.291	1.663
μ / mm^{-1}	2.398	1.342
Crystal size / mm	0.03x0.03x0.08	0.04x0.08x0.14
Tmin/max	0.810/1.000	0.7069/0.893845
θ_{max}	28.034	26.998
Refl. collected	15477	9891
Unique refl.	2427	3975
R_{int}	0.0205	0.0768
Refl. [$F_o > 4\sigma(F_o)$]	2276	3365
Parameters	106	179
$R_1[F_o > 4\sigma(F_o)]$	0.0198	0.0581
wR_2 (for all data)	0.0493	0.1578
GOF	1.122	1.025
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / eÅ^{-3}	0.952, -0.305	1.141, -0.937

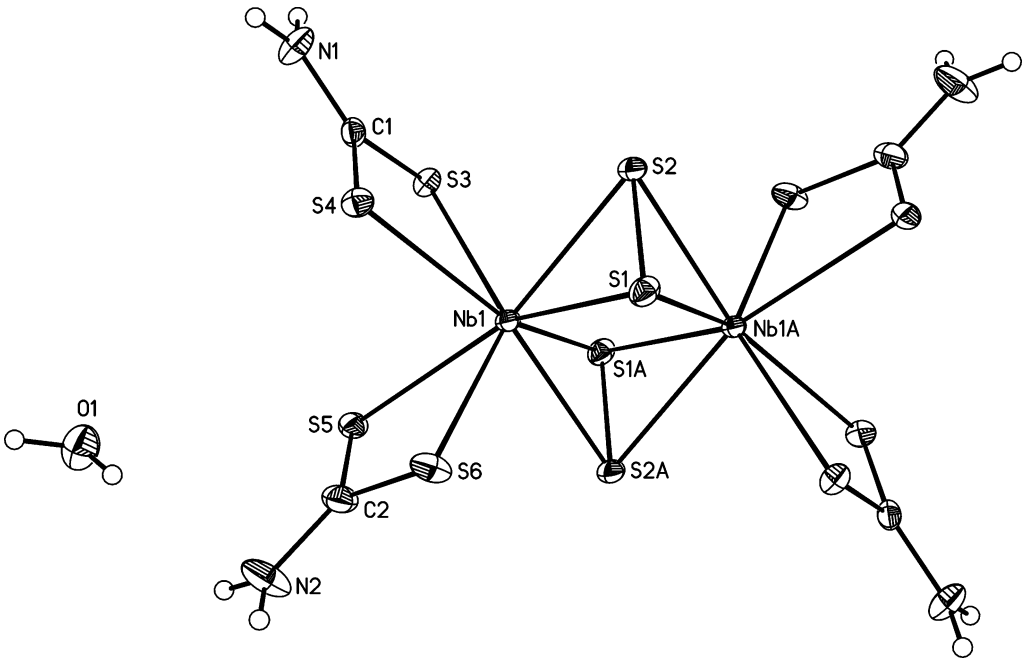

Figure S7. Crystal structure of compound **1** with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry transformations: A: -x+1,-y+1,-z.

Table S3. Bond lengths [Å] and angles [°] for compound **1**. Symmetry transformations: A: -x+1,-y+1,-z.

Nb(1)-S(1)	2.5134(5)	Nb(1)-S(3)	2.5945(5)
Nb(1)-S(1)#1	2.5105(6)	Nb(1)-S(4)	2.6266(5)
Nb(1)-S(2)#1	2.4941(5)	Nb(1)-S(5)	2.6217(5)
Nb(1)-S(2)	2.4894(5)	Nb(1)-S(6)	2.5783(6)
Nb(1)-Nb(1)#1	2.8650(4)		
S(1)#1-Nb(1)-S(1)	110.459(15)	S(2)-Nb(1)-S(3)	81.376(18)
S(1)-Nb(1)-S(3)	126.801(18)	S(2)#1-Nb(1)-S(3)	126.219(18)
S(1)#1-Nb(1)-S(3)	80.712(17)	S(2)-Nb(1)-S(4)	84.224(17)
S(1)-Nb(1)-S(4)	89.601(17)	S(2)#1-Nb(1)-S(4)	161.000(18)
S(1)#1-Nb(1)-S(4)	147.836(18)	S(2)#1-Nb(1)-S(5)	82.952(17)
S(1)#1-Nb(1)-S(5)	88.535(17)	S(2)-Nb(1)-S(5)	161.918(18)
S(1)-Nb(1)-S(5)	147.707(18)	S(2)#1-Nb(1)-S(6)	81.991(19)
S(1)-Nb(1)-S(6)	80.251(18)	S(2)-Nb(1)-S(6)	125.571(19)
S(1)#1-Nb(1)-S(6)	127.440(19)	S(3)-Nb(1)-S(4)	67.125(17)
S(2)#1-Nb(1)-S(1)	90.736(18)	S(3)-Nb(1)-S(5)	80.699(17)
S(2)-Nb(1)-S(1)#1	90.912(18)	S(5)-Nb(1)-S(4)	86.650(17)
S(2)-Nb(1)-S(1)	47.933(18)	S(6)-Nb(1)-S(3)	134.816(19)
S(2)#1-Nb(1)-S(1)#1	47.916(18)	S(6)-Nb(1)-S(4)	79.346(18)
S(2)-Nb(1)-S(2)#1	109.814(15)	S(6)-Nb(1)-S(5)	67.529(17)

Table S4. Hydrogen bonds [Å and °] for compound **1**. Symmetry transformations used to generate equivalent atoms: #3 x-1/2,-y+1/2,-z+1; #4 -x,-y+1,-z+1; #5 x,-y+1,z-1/2; #6 -x+1/2,-y+1/2,z-1/2

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...S(6)#3	0.88	2.68	3.516(2)	159.1
N(1)-H(1B)...S(5)#4	0.88	2.88	3.320(2)	112.6
N(1)-H(1B)...O(1)#4	0.88	2.45	3.173(5)	140.1
N(2)-H(2A)...S(3)#5	0.88	2.60	3.349(2)	143.2
N(2)-H(2B)...S(4)#6	0.88	2.83	3.348(2)	119.1
O(1)-H(1)...N(2)	0.84	2.29	2.962(3)	137.7

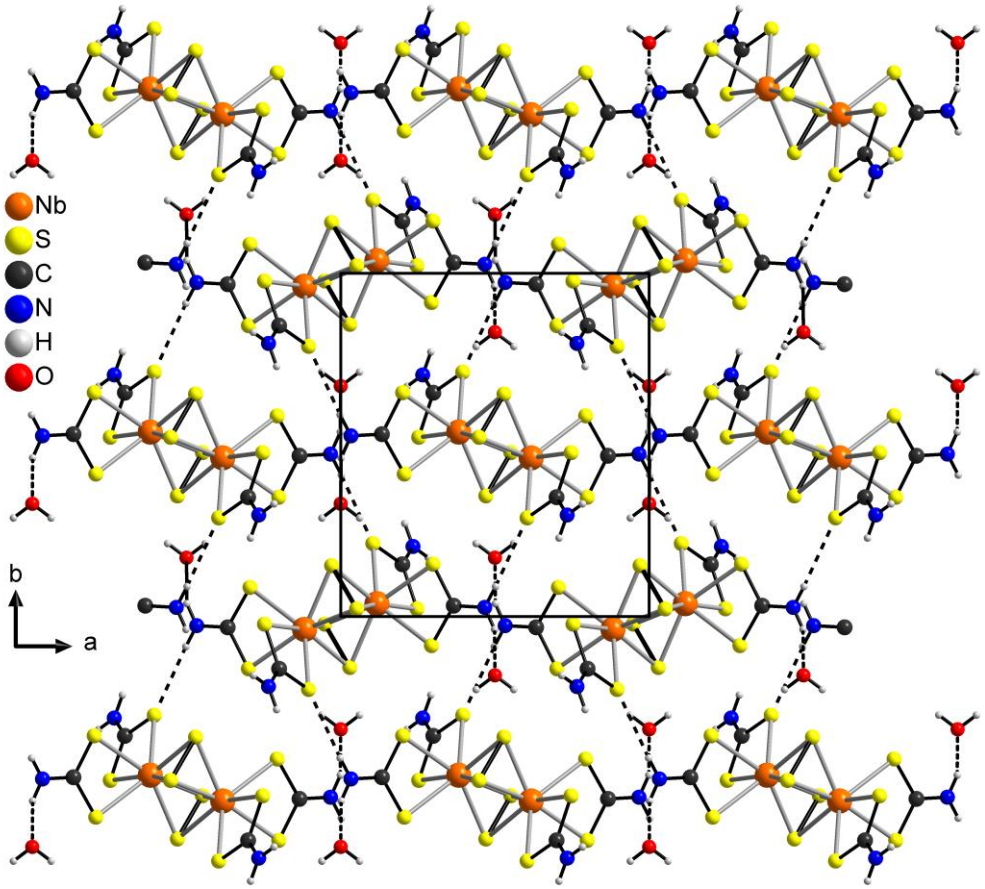

Figure S8. Crystal structure of compound **1** with view along the crystallographic *c* axis and intermolecular hydrogen bonding shown as dashed lines.

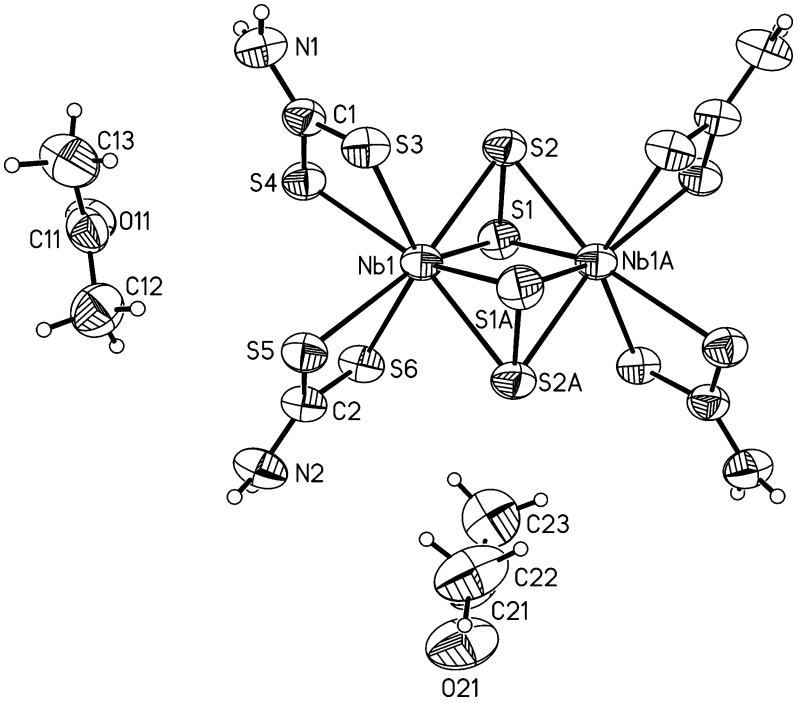

Figure S9. Crystal structure of compound **1-Acetone** with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry transformations: -x+1,-y+1,-z+1.

Table S5. Bond lengths [Å] and angles [°] for compound **1-Acetone**. Symmetry transformations: -x+1,-y+1,-z+1.

Nb(1)-S(2)	2.4884(12)	Nb(1)-S(6)	2.5667(12)
Nb(1)-S(2A)	2.4990(12)	Nb(1)-S(3)	2.5765(12)
Nb(1)-S(1A)	2.5026(12)	Nb(1)-S(4)	2.6104(12)
Nb(1)-S(1)	2.5062(12)	Nb(1)-S(5)	2.6252(12)
Nb(1)-Nb(1A)	2.8693(8)		
S(2)-Nb(1)-S(2A)	109.76(3)	S(6)-Nb(1)-S(3)	136.80(4)
S(2)-Nb(1)-S(1A)	91.00(4)	S(2)-Nb(1)-S(4)	84.00(4)
S(2A)-Nb(1)-S(1A)	47.61(4)	S(2A)-Nb(1)-S(4)	161.58(4)
S(2)-Nb(1)-S(1)	47.68(4)	S(1A)-Nb(1)-S(4)	147.53(4)
S(2A)-Nb(1)-S(1)	90.67(4)	S(1)-Nb(1)-S(4)	89.99(4)
S(1A)-Nb(1)-S(1)	110.10(3)	S(6)-Nb(1)-S(4)	79.70(4)
S(2)-Nb(1)-S(6)	124.36(4)	S(3)-Nb(1)-S(4)	67.77(4)
S(2A)-Nb(1)-S(6)	82.34(4)	S(2)-Nb(1)-S(5)	162.43(4)
S(1A)-Nb(1)-S(6)	127.81(4)	S(2A)-Nb(1)-S(5)	83.45(4)
S(1)-Nb(1)-S(6)	79.35(4)	S(1A)-Nb(1)-S(5)	89.76(4)
S(2)-Nb(1)-S(3)	80.73(4)	S(1)-Nb(1)-S(5)	146.82(4)
S(2A)-Nb(1)-S(3)	125.21(4)	S(6)-Nb(1)-S(5)	67.52(4)
S(1A)-Nb(1)-S(3)	79.76(4)	S(3)-Nb(1)-S(5)	82.14(4)
S(1)-Nb(1)-S(3)	126.34(4)	S(4)-Nb(1)-S(5)	85.96(4)

Table S6. Hydrogen bonds [Å and °] for compound **1-Acetone**. Symmetry transformations: #2 x-1,y,z; #3 x-1,y+1,z; #4 -x+1,-y+1,-z+1; #5 x+1,y,z; #6 -x+1,-y+2,-z+1.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...S(5)#2	0.88	2.56	3.439(5)	175.6
N(1)-H(2)...O(21)#3	0.88	2.03	2.897(7)	169.8
N(2)-H(3)...O(11)#4	0.88	2.10	2.901(6)	150.9
N(2)-H(4)...O(11)#5	0.88	2.08	2.894(6)	153.7
C(12)-H(12B)...S(5)	0.98	2.93	3.822(7)	151.1
C(13)-H(13C)...S(5)#6	0.98	2.96	3.567(7)	120.9

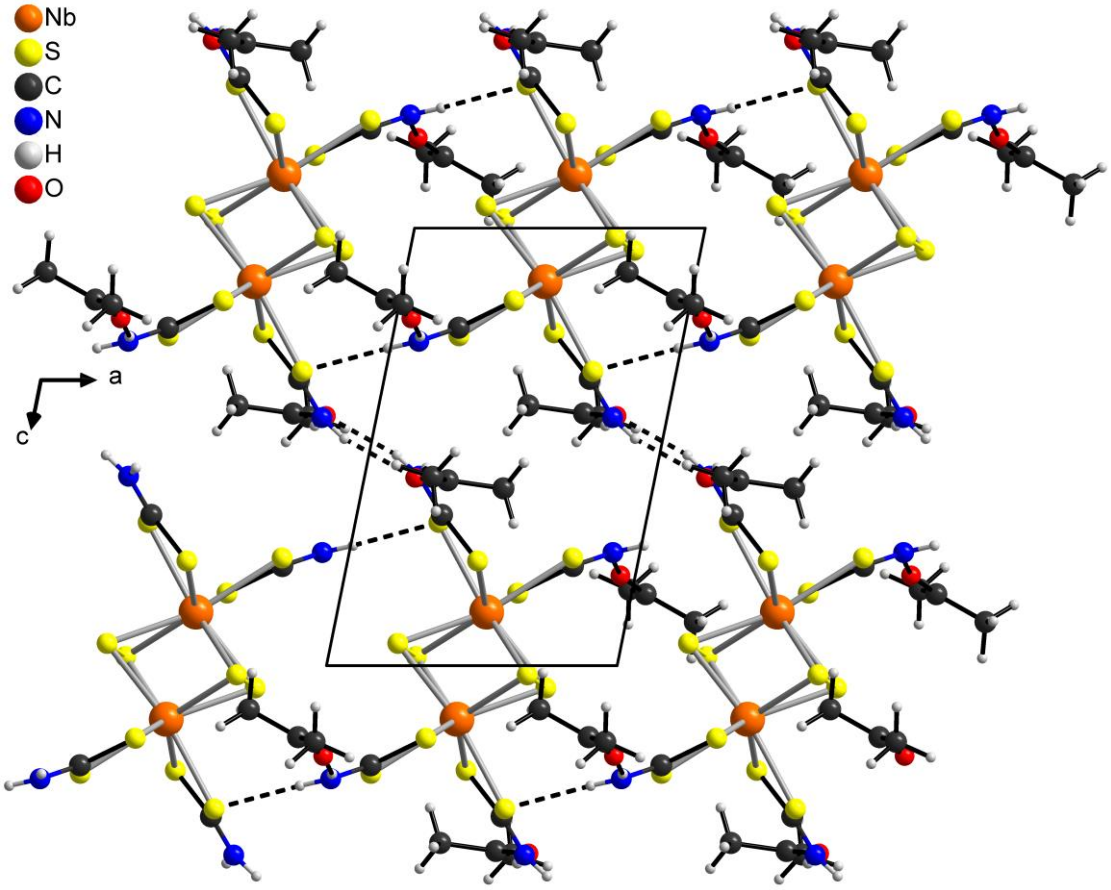

Figure S10. Crystal structure of compound **1-Acetone** with view along the crystallographic *b* axis and intermolecular hydrogen bonding shown as dashed lines.

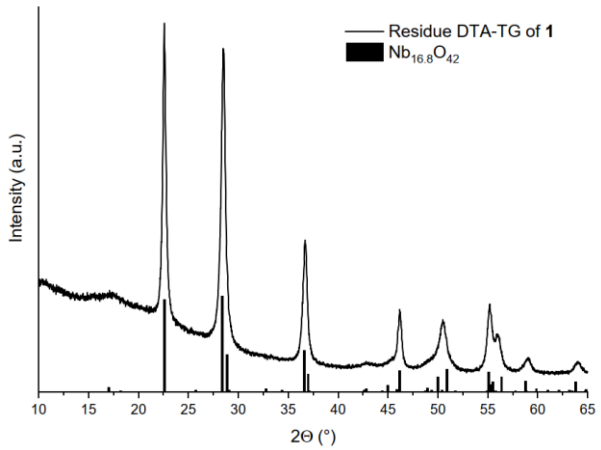

Figure S11: Comparison of the XRPD pattern of the residue of **1** after heating to 600 °C in the DTA-TG experiment. Tick marks are shown for the calculated pattern of $Nb_{16.8}O_{42}$.[47]

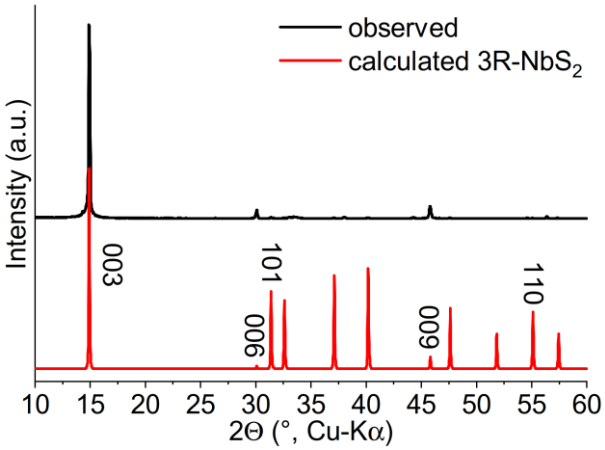

Figure S12: XRPD pattern recorded in reflection geometry of the decomposition product of **1** on a Si/SiO_2 substrate synthesized at 1000 °C in a sealed quartz tube. For comparison the calculated pattern for 3R-NbS_2[48] is shown. A strong preferred orientation towards the 00*l* reflections is evident, which is (for reflection geometry) in line with the layers growing in parallel to the sample surface. Selected Miller indices are shown to highlight the strong preferred orientation of the crystallites on the substrate surface.

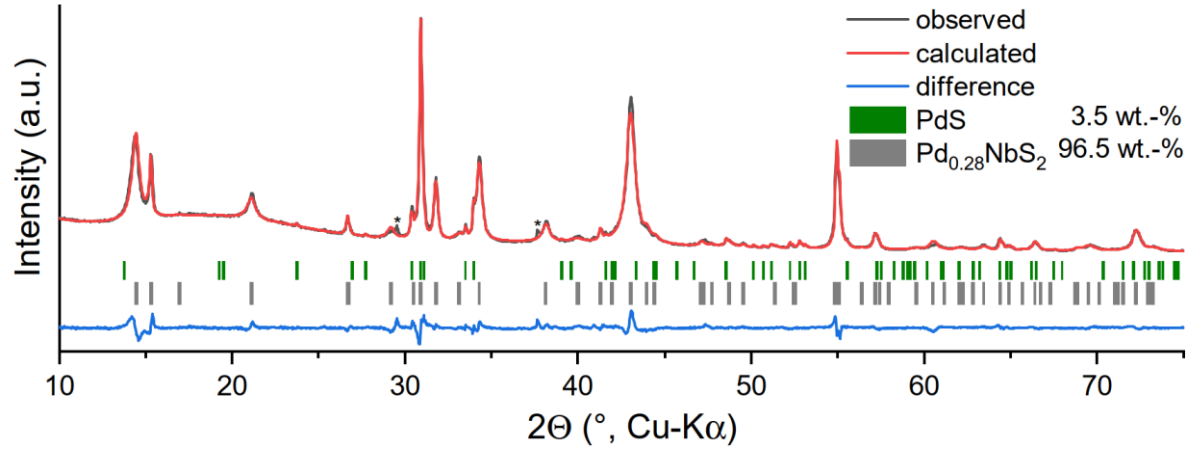

Figure S13: Difference plot of the Rietveld refinement of the product obtained after co-decomposition of **1** and $Pd(CS_2NH_2)_2$. Unidentified reflections are marked with an asterisk.

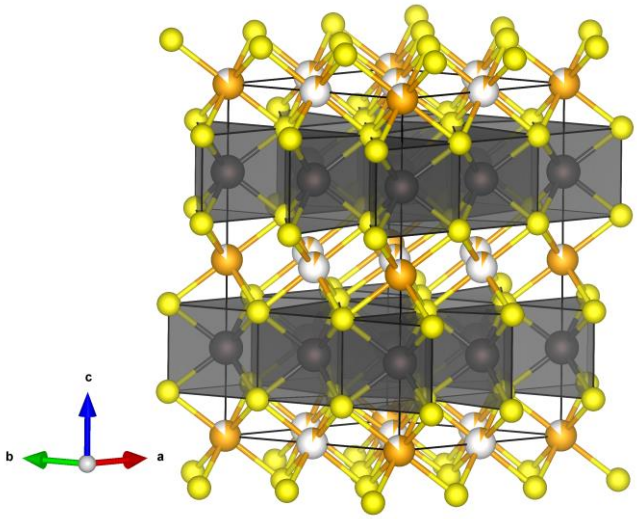

Figure S14: Depiction of the unit cell of $Pd_{0.28}NbS_2$. Occupancies smaller than one are shown with partially filled spheres. Color code: Pd (orange), Nb (black) and S (yellow).

Table S7: Details of the crystal structure of $Pd_{0.28}NbS_2$.

Formula	$Pd_{0.28}NbS_2$
Molecular weight, g mol^{-1}	186.84
Crystal system	hexagonal
Space group	$P6_3/mmc$
a, Å	6.6755(1)
b, Å	6.6755(1)
c, Å	12.2298(8)
α, °	90
β, °	90
γ, °	120
Cell volume, Å^3	471.97(3)
T, K	298(2)
Z	8
D_{calc}, g cm^{-1}	5.245(6)
R_{wp}, %	5.5
R_{exp}, %	1.9
gof	2.96
R_{Bragg}, %	1.30

Table S8: Atomic sites of the crystal structure of $Pd_{0.28}NbS_2$.

Atom	Wyckoff site	x	y	z	Occupancy	B_{iso} / Å^2
Nb1	2*b*	0	0	0.25	1	2.24(6)
Nb2	6*h*	0.4928(4)	0.9857(8)	0.25	1	2.24(6)
Pd1	2*a*	0	0	0	0.863(6)	3.0(2)
Pd2	6*g*	0.5	0	0	0.081(2)	3.0(2)
S1	4*f*	1/3	2/3	0.113(1)	1	2.04(8)
S2	12*k*	0.8285(4)	0.6569(8)	0.3744(4)	1	2.04(8)