Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

$[Ge_2S_6]^{4-}$ $[Co(dien)_2]^{2+}$ $[dienH_2]^{2+}$

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Content

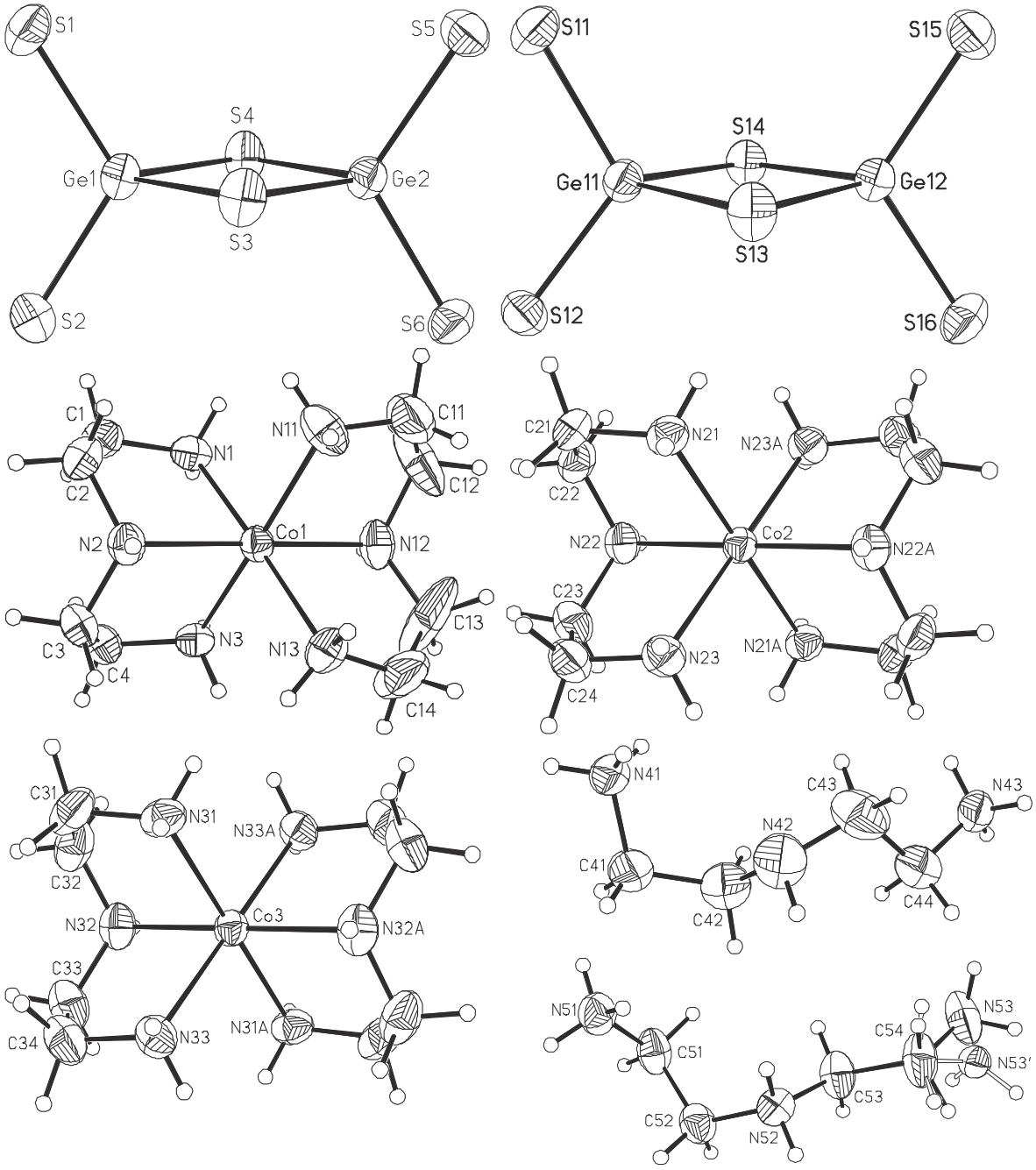

Figure S1. Part of the crystal structure of compound **1** with labeling and displacement ellipsoids drawn at the 50% probability level.

Table S1. Selected bond lengths [Å] and angles [°] for compound 1. Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1 #2 -x+1,-y,-z+1

Ge(1)-S(1)	2.1521(10)	Ge(11)-S(11)	2.1556(9)
Ge(1)-S(2)	2.1559(9)	Ge(11)-S(12)	2.1568(9)
Ge(1)-S(4)	2.2658(9)	Ge(11)-S(13)	2.2697(9)
Ge(1)-S(3)	2.2862(9)	Ge(11)-S(14)	2.2762(8)
Ge(2)-S(6)	2.1569(9)	Ge(12)-S(15)	2.1554(9)
Ge(2)-S(5)	2.1643(9)	Ge(12)-S(16)	2.1576(9)
Ge(2)-S(4)	2.2701(9)	Ge(12)-S(14)	2.2740(9)
Ge(2)-S(3)	2.2727(8)	Ge(12)-S(13)	2.2858(9)
S(1)-Ge(1)-S(2)	116.67(4)	S(11)-Ge(11)-S(12)	114.38(4)
S(1)-Ge(1)-S(4)	112.55(4)	S(11)-Ge(11)-S(13)	112.70(4)
S(2)-Ge(1)-S(4)	112.73(4)	S(12)-Ge(11)-S(13)	113.56(3)
S(1)-Ge(1)-S(3)	107.70(4)	S(11)-Ge(11)-S(14)	108.97(4)
S(2)-Ge(1)-S(3)	111.17(4)	S(12)-Ge(11)-S(14)	111.71(4)
S(4)-Ge(1)-S(3)	93.50(3)	S(13)-Ge(11)-S(14)	93.60(3)
S(6)-Ge(2)-S(5)	115.92(4)	S(15)-Ge(12)-S(16)	115.66(4)
S(6)-Ge(2)-S(4)	111.47(4)	S(15)-Ge(12)-S(14)	114.01(4)
S(5)-Ge(2)-S(4)	111.80(4)	S(16)-Ge(12)-S(14)	111.14(4)
S(6)-Ge(2)-S(3)	110.89(4)	S(15)-Ge(12)-S(13)	111.04(4)
S(5)-Ge(2)-S(3)	110.89(3)	S(16)-Ge(12)-S(13)	109.50(4)
S(4)-Ge(2)-S(3)	93.75(3)	S(14)-Ge(12)-S(13)	93.23(3)
Ge(2)-S(3)-Ge(1)	86.09(3)	Ge(11)-S(13)-Ge(12)	86.44(3)
Ge(1)-S(4)-Ge(2)	86.63(3)	Ge(12)-S(14)-Ge(11)	86.57(3)
Co(1)-N(2)	2.159(3)	Co(1)-N(13)	2.168(3)
Co(1)-N(3)	2.167(3)	Co(1)-N(1)	2.173(3)
Co(1)-N(12)	2.168(3)	Co(1)-N(11)	2.188(3)
N(2)-Co(1)-N(3)	81.45(11)	N(12)-Co(1)-N(1)	99.61(12)
N(2)-Co(1)-N(12)	179.56(12)	N(13)-Co(1)-N(1)	176.78(12)
N(3)-Co(1)-N(12)	98.59(12)	N(2)-Co(1)-N(11)	99.81(12)
N(2)-Co(1)-N(13)	99.17(11)	N(3)-Co(1)-N(11)	175.67(12)
N(3)-Co(1)-N(13)	88.15(12)	N(12)-Co(1)-N(11)	80.17(13)
N(12)-Co(1)-N(13)	80.40(12)	N(13)-Co(1)-N(11)	95.71(13)
N(2)-Co(1)-N(1)	80.82(11)	N(1)-Co(1)-N(11)	87.45(13)
N(3)-Co(1)-N(1)	88.67(11)		
Co(2)-N(22)	2.140(3)	Co(3)-N(32)	2.141(3)
Co(2)-N(22)#1	2.140(3)	Co(3)-N(32)#2	2.141(3)
Co(2)-N(21)	2.160(3)	Co(3)-N(31)#2	2.165(3)
Co(2)-N(21)#1	2.160(3)	Co(3)-N(31)	2.165(3)
Co(2)-N(23)#1	2.184(3)	Co(3)-N(33)	2.197(3)
Co(2)-N(23)	2.184(3)	Co(3)-N(33)#2	2.197(3)
N(22)-Co(2)-N(22)#1	180.000(1)	N(32)-Co(3)-N(32)#2	180.0
N(22)-Co(2)-N(21)	81.81(11)	N(32)-Co(3)-N(31)#2	98.05(12)
N(22)#1-Co(2)-N(21)	98.19(11)	N(32)#2-Co(3)-N(31)#2	81.95(12)
N(22)-Co(2)-N(21)#1	98.19(11)	N(32)-Co(3)-N(31)	81.95(12)
N(22)#1-Co(2)-N(21)#1	81.81(11)	N(32)#2-Co(3)-N(31)	98.05(12)
N(21)-Co(2)-N(21)#1	180.0	N(31)#2-Co(3)-N(31)	180.00(16)
N(22)-Co(2)-N(23)#1	98.60(11)	N(32)-Co(3)-N(33)	80.64(11)
N(22)#1-Co(2)-N(23)#1	81.40(11)	N(32)#2-Co(3)-N(33)	99.36(11)
N(21)-Co(2)-N(23)#1	89.60(11)	N(31)#2-Co(3)-N(33)	88.91(11)
N(21)#1-Co(2)-N(23)#1	90.40(11)	N(31)-Co(3)-N(33)	91.09(11)
N(22)-Co(2)-N(23)	81.40(11)	N(32)-Co(3)-N(33)#2	99.36(11)
N(22)#1-Co(2)-N(23)	98.60(11)	N(32)#2-Co(3)-N(33)#2	80.64(11)
N(21)-Co(2)-N(23)	90.40(11)	N(31)#2-Co(3)-N(33)#2	91.09(11)
N(21)#1-Co(2)-N(23)	89.60(11)	N(31)-Co(3)-N(33)#2	88.91(11)
N(23)#1-Co(2)-N(23)	180.00(17)	N(33)-Co(3)-N(33)#2	180.00(13)

Table S2. Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 140° for compound **1**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1N	0.900	2.521	157.28	3.370	S6 [x+1, y-1, z]
N1-H2N	0.900	2.489	163.60	3.362	S2 [-x+1, -y+1, -z]
N2-H3N	0.910	2.826	144.65	3.606	S4 [-x, -y+1, -z]
N3-H4N	0.900	2.660	149.18	3.464	S2 [-x+1, -y+1, -z]
N3-H5N	0.900	2.536	148.89	3.339	S1
N11-H7N	0.900	2.855	148.08	3.650	S5 [-x, -y+1, -z]
N12-H8N	0.910	2.778	147.06	3.576	S1 [-x+1, -y+1, -z]
N12-H8N	0.910	2.943	134.68	3.641	S3 [-x+1, -y+1, -z]
N13-H9N	0.900	2.826	165.53	3.704	S5 [-x, -y+1, -z]
N13-H10N	0.900	2.775	148.49	3.573	S1
N21-H11N	0.900	2.854	147.29	3.644	S15 [-x, -y+1, -z+1]
N21-H12N	0.900	2.547	147.81	3.343	S11 [-x+1, -y+1, -z+1]
N22-H13N	0.910	2.658	147.23	3.459	S16 [x+1, y, z]
N23-H14N	0.900	2.585	168.82	3.473	S11
N23-H15N	0.900	2.876	148.12	3.671	S15 [-x, -y+1, -z+1]
N31-H16N	0.900	2.624	149.93	3.433	S12
N31-H17N	0.900	2.588	159.30	3.444	S16 [x+1, y, z]
N32-H18N	0.910	2.643	150.02	3.461	S11 [-x+1, -y, -z+1]
N33-H19N	0.900	2.656	160.52	3.517	S16 [-x, -y, -z+1]
N33-H20N	0.900	2.797	148.11	3.593	S12
N41-H21N	0.890	2.445	159.39	3.293	S6
N41-H22N	0.890	2.641	166.13	3.511	S6 [-x, -y+2, -z]
N41-H23N	0.890	2.442	177.65	3.332	S2
N42-H24N	0.900	2.711	158.01	3.562	S15 [x, y+1, z-1]
N43-H25N	0.890	1.995	163.29	2.859	N53_a [-x, -y+1, -z]
N43-H25N	0.890	2.107	169.67	2.987	N53'_b [-x, -y+1, -z]
N43-H26N	0.890	2.377	165.21	3.246	S16 [-x, -y+1, -z]
N43-H27N	0.890	2.380	169.34	3.258	S12 [-x, -y+1, -z]
N51-H28N	0.890	2.421	156.32	3.255	S15 [-x, -y+1, -z+1]
N51-H29N	0.890	2.262	172.17	3.146	S11 [-x, -y+1, -z+1]
N51-H30N	0.890	2.558	156.75	3.394	S5
N52-H31N	0.900	2.340	174.69	3.237	S5
N52-H32N	0.900	2.296	172.78	3.191	S1
N53'-H33N	0.887	2.572	149.73	3.368	S2 [-x, -y+1, -z]
N53'-H35N_b	0.890	2.538	170.16	3.419	S4 [-x, -y+1, -z]

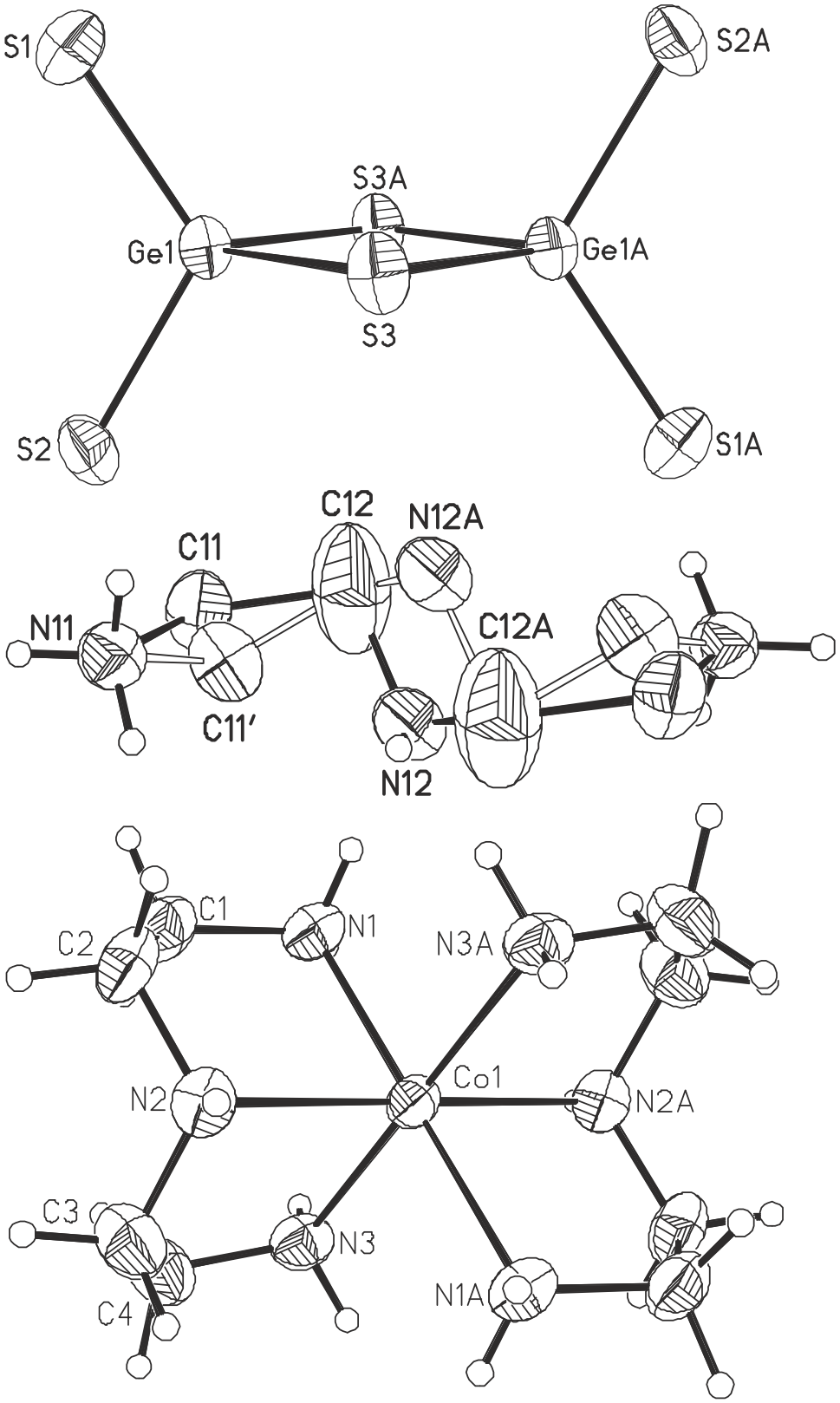

Figure S2. Part of the crystal structure of compound **2** with labeling and displacement ellipsoids drawn at the 50% probability level. Please note: For the uncoordinated amine molecules the C-H H atoms are omitted for clarity.

Table S3. Selected bond lengths [Å] and angles [°] for compound **2**. Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+2 #2 -x+1,-y+1,-z+1 #3 -x+2,-y,-z+2

Ge(1)-S(1)	2.1416(8)	Ge(1)-S(3)	2.2762(7)
Ge(1)-S(2)	2.1572(7)	Ge(1)-S(3)#1	2.2783(7)
S(1)-Ge(1)-S(2)	116.37(3)	S(1)-Ge(1)-S(3)#1	112.05(3)
S(1)-Ge(1)-S(3)	112.35(3)	S(2)-Ge(1)-S(3)#1	110.02(3)
S(2)-Ge(1)-S(3)	110.11(3)	S(3)-Ge(1)-S(3)#1	93.68(2)
Co(1)-N(3)	2.153(2)	Co(1)-N(2)	2.163(2)
Co(1)-N(3)#2	2.153(2)	Co(1)-N(1)#2	2.188(2)
Co(1)-N(2)#2	2.163(2)	Co(1)-N(1)	2.188(2)
N(3)-Co(1)-N(3)#2	180.000(1)	N(2)#2-Co(1)-N(1)#2	81.16(9)
N(3)-Co(1)-N(2)#2	99.45(9)	N(2)-Co(1)-N(1)#2	98.84(9)
N(3)#2-Co(1)-N(2)#2	80.55(9)	N(3)-Co(1)-N(1)	90.59(9)
N(3)-Co(1)-N(2)	80.55(9)	N(3)#2-Co(1)-N(1)	89.41(9)
N(3)#2-Co(1)-N(2)	99.45(9)	N(2)#2-Co(1)-N(1)	98.84(9)
N(2)#2-Co(1)-N(2)	180.00(10)	N(2)-Co(1)-N(1)	81.16(9)
N(3)-Co(1)-N(1)#2	89.41(9)	N(1)#2-Co(1)-N(1)	180.0
N(3)#2-Co(1)-N(1)#2	90.59(9)		

Table S4. Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 140° for compound **2**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1N	0.900	2.868	145.76	3.647	S2 [x-1, y, z]
N2-H3N	0.910	2.673	145.49	3.461	S3
N3-H4N	0.900	2.458	163.71	3.331	S1 [-x+1, -y+1, -z+1]
N3-H5N	0.900	2.449	175.19	3.347	S2 [-x+2, -y+1, -z+1]
N11-H6N	0.900	2.496	173.39	3.392	S1 [-x+1, -y+1, -z+2]
N11-H7N	0.900	2.430	166.13	3.311	S2
N11-H8N	0.900	2.692	175.56	3.590	S2 [-x+2, -y+1, -z+2]

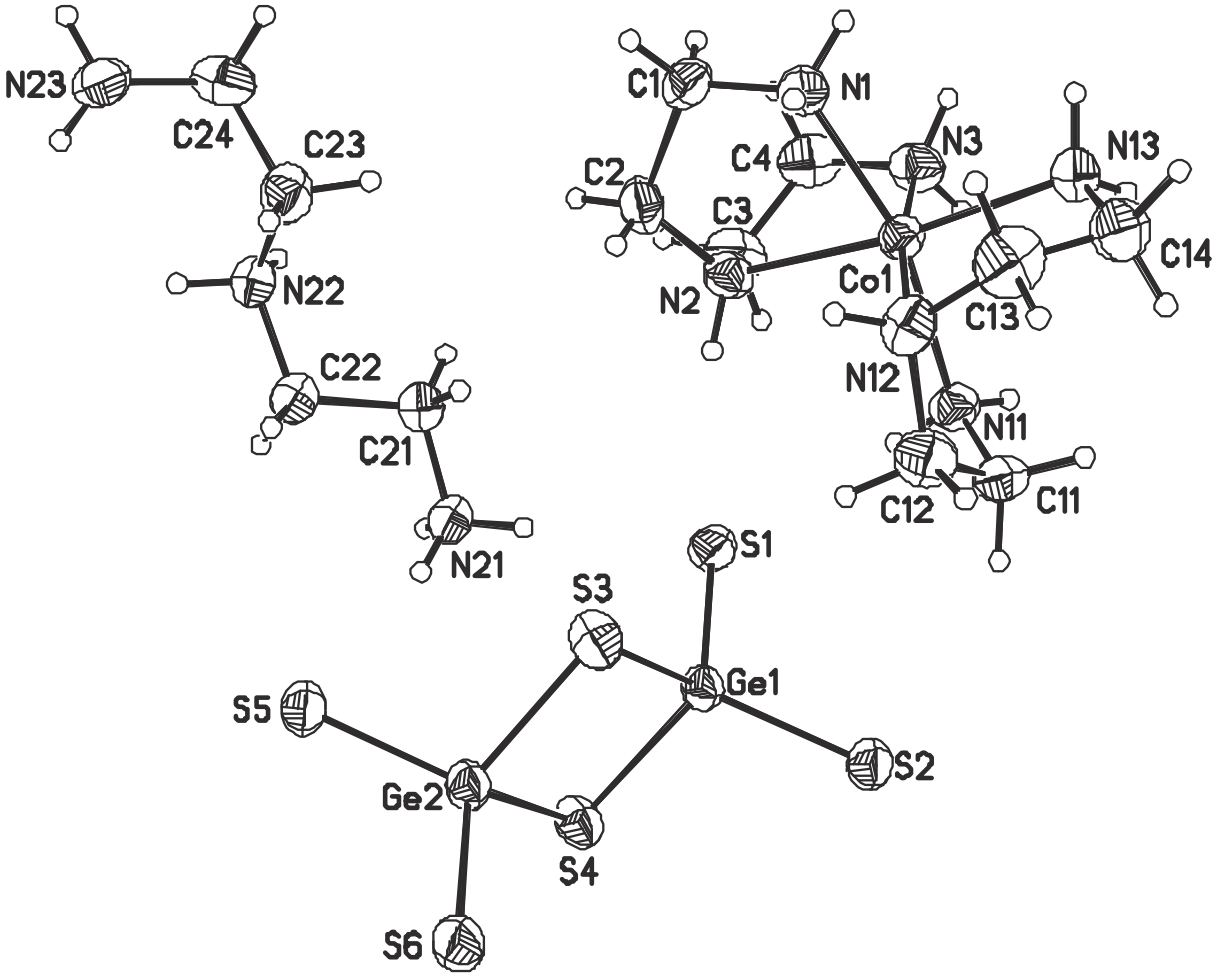

Figure S3. Part of the crystal structure of compound **3** with labeling and displacement ellipsoids drawn at the 50% probability level.

Table S5. Selected bond lengths [Å] and angles [°] for compound **3**.

Ge(1)-S(2)	2.1608(10)	Ge(2)-S(5)	2.1522(10)
Ge(1)-S(1)	2.1621(10)	Ge(2)-S(6)	2.1714(10)
Ge(1)-S(3)	2.2664(10)	Ge(2)-S(4)	2.2797(11)
Ge(1)-S(4)	2.2701(10)	Ge(2)-S(3)	2.2878(11)
S(2)-Ge(1)-S(1)	113.18(4)	S(5)-Ge(2)-S(6)	115.70(4)
S(2)-Ge(1)-S(3)	113.09(4)	S(5)-Ge(2)-S(4)	113.09(4)
S(1)-Ge(1)-S(3)	110.48(4)	S(6)-Ge(2)-S(4)	111.53(4)
S(2)-Ge(1)-S(4)	110.99(4)	S(5)-Ge(2)-S(3)	110.03(4)
S(1)-Ge(1)-S(4)	114.14(4)	S(6)-Ge(2)-S(3)	111.56(4)
S(3)-Ge(1)-S(4)	93.48(4)	S(4)-Ge(2)-S(3)	92.66(4)
Ge(1)-S(3)-Ge(2)	86.86(4)	Ge(1)-S(4)-Ge(2)	86.97(4)
Co(1)-N(3)	2.139(3)	Co(1)-N(1)	2.155(3)
Co(1)-N(11)	2.145(3)	Co(1)-N(12)	2.205(3)
Co(1)-N(13)	2.150(3)	Co(1)-N(2)	2.210(3)
N(3)-Co(1)-N(11)	95.12(13)	N(13)-Co(1)-N(12)	80.31(13)
N(3)-Co(1)-N(13)	94.40(13)	N(1)-Co(1)-N(12)	88.68(12)
N(11)-Co(1)-N(13)	96.22(13)	N(3)-Co(1)-N(2)	80.44(12)
N(3)-Co(1)-N(1)	97.21(13)	N(11)-Co(1)-N(2)	89.68(12)
N(11)-Co(1)-N(1)	162.35(13)	N(13)-Co(1)-N(2)	172.51(13)
N(13)-Co(1)-N(1)	95.37(12)	N(1)-Co(1)-N(2)	80.01(12)
N(3)-Co(1)-N(12)	172.46(13)	N(12)-Co(1)-N(2)	105.32(12)
N(11)-Co(1)-N(12)	80.22(12)		

Table S6. Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 140° for compound **3**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1N	0.900	2.699	161.51	3.564	S6 [x-1/2, y, -z+3/2]
N1-H2N	0.900	2.751	141.08	3.498	S2 [x-1/2, -y+3/2, -z+1]
N2-H3N	0.910	2.743	142.36	3.508	S1
N3-H4N	0.900	2.677	142.56	3.436	S2 [x-1/2, -y+3/2, -z+1]
N3-H5N	0.900	2.656	159.02	3.511	S6 [x, -y+3/2, z-1/2]
N11-H6N	0.900	2.753	175.59	3.651	S1
N11-H7N	0.900	2.741	142.58	3.498	S5 [x, -y+3/2, z-1/2]
N13-H9N	0.900	2.737	151.41	3.554	S5 [x, -y+3/2, z-1/2]
N13-H10N	0.900	2.633	155.27	3.471	S1 [x-1/2, -y+3/2, -z+1]
N21-H11N	0.890	2.357	168.04	3.233	S5
N21-H12N	0.890	2.327	177.77	3.216	S1
N21-H13N	0.890	1.917	171.22	2.800	N23 [x+1/2, y, -z+3/2]
N22-H14N	0.900	2.240	164.98	3.118	S2 [-x+1, y-1/2, -z+3/2]
N22-H15N	0.900	2.340	169.69	3.230	S6 [-x+1, y-1/2, -z+3/2]
N23-H16N	0.890	2.585	164.34	3.451	S2 [-x+1, y-1/2, -z+3/2]
N23-H17N	0.890	2.577	171.27	3.459	S3 [-x+1/2, y-1/2, z]

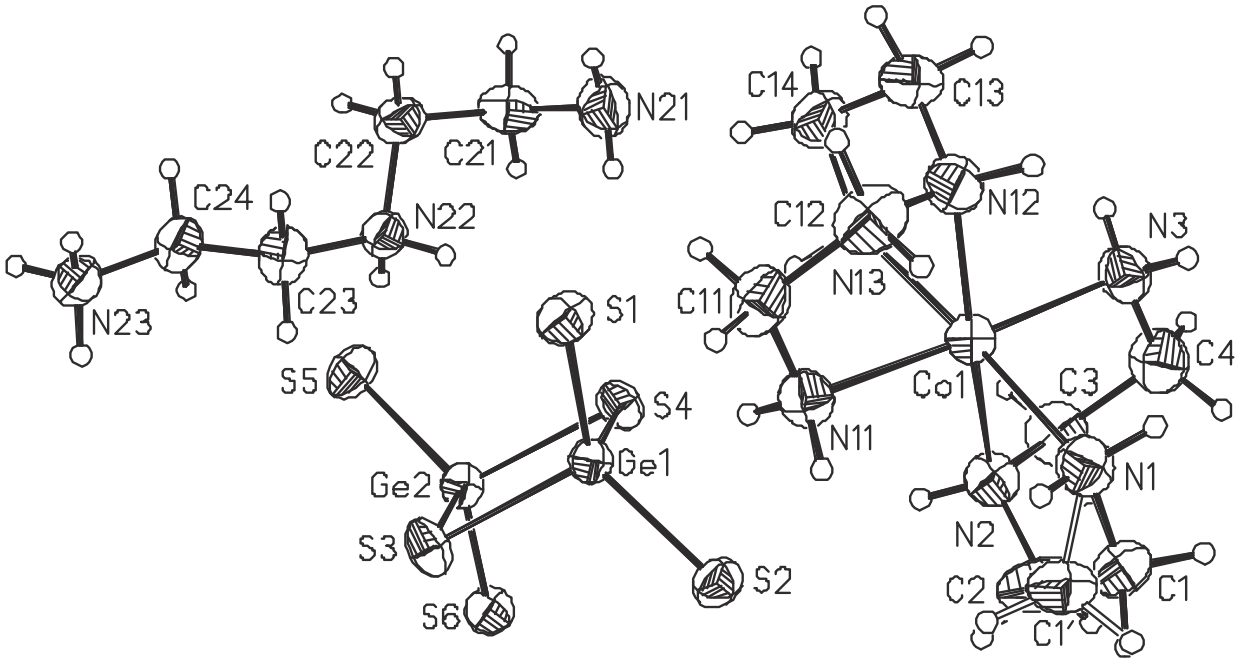

Figure S4. Part of the crystal structure of compound **4** with labeling and displacement ellipsoids drawn at the 50% probability level.

Table S7. Selected bond lengths [Å] and angles [°] for compound**4**.

Ge(1)-S(1)	2.1592(7)	Ge(2)-S(5)	2.1519(7)
Ge(1)-S(2)	2.1604(7)	Ge(2)-S(6)	2.1570(7)
Ge(1)-S(3)	2.2694(6)	Ge(2)-S(3)	2.2822(7)
Ge(1)-S(4)	2.2737(7)	Ge(2)-S(4)	2.2975(7)
S(1)-Ge(1)-S(2)	113.12(3)	S(5)-Ge(2)-S(6)	115.18(3)
S(1)-Ge(1)-S(3)	112.45(3)	S(5)-Ge(2)-S(3)	113.25(3)
S(2)-Ge(1)-S(3)	111.18(3)	S(6)-Ge(2)-S(3)	111.77(3)
S(1)-Ge(1)-S(4)	112.51(3)	S(5)-Ge(2)-S(4)	110.84(3)
S(2)-Ge(1)-S(4)	112.88(3)	S(6)-Ge(2)-S(4)	111.39(3)
S(3)-Ge(1)-S(4)	93.16(2)	S(3)-Ge(2)-S(4)	92.20(2)
Ge(1)-S(3)-Ge(2)	87.55(2)	Ge(1)-S(4)-Ge(2)	87.07(2)
Co(1)-N(12)	2.132(2)	Co(1)-N(3)	2.183(2)
Co(1)-N(2)	2.146(2)	Co(1)-N(13)	2.194(2)
Co(1)-N(11)	2.178(2)	Co(1)-N(1)	2.196(2)
N(12)-Co(1)-N(2)	177.86(9)	N(11)-Co(1)-N(13)	88.62(9)
N(12)-Co(1)-N(11)	81.14(9)	N(3)-Co(1)-N(13)	89.41(9)
N(2)-Co(1)-N(11)	100.99(9)	N(12)-Co(1)-N(1)	100.03(9)
N(12)-Co(1)-N(3)	97.22(9)	N(2)-Co(1)-N(1)	80.19(9)
N(2)-Co(1)-N(3)	80.64(9)	N(11)-Co(1)-N(1)	88.95(9)
N(11)-Co(1)-N(3)	177.62(9)	N(3)-Co(1)-N(1)	93.06(9)
N(12)-Co(1)-N(13)	81.17(10)	N(13)-Co(1)-N(1)	177.09(9)
N(2)-Co(1)-N(13)	98.71(9)		

Table S8. Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 140° for compound **4**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1N_a	0.900	2.873	142.14	3.626	S5 [-x+1, -y+1, z-1/2]
N1-H2N_a	0.900	2.822	164.38	3.696	S6 [-x+1/2, y, z-1/2]
N1-H1NA_b	0.900	2.729	174.29	3.626	S5 [-x+1, -y+1, z-1/2]
N2-H3N	0.910	2.550	157.38	3.408	S2
N3-H4N	0.900	2.725	167.66	3.609	S2 [x+1/2, -y+1, z]
N3-H5N	0.900	2.891	144.60	3.662	S5 [-x+1, -y+1, z-1/2]
N11-H6N	0.900	2.771	144.04	3.539	S1
N11-H7N	0.900	2.541	157.89	3.392	S6 [-x+1/2, y, z-1/2]
N12-H8N	0.910	2.549	156.77	3.405	S6 [-x+1, -y+1, z-1/2]
N13-H9N	0.900	2.637	144.39	3.409	S2 [x+1/2, -y+1, z]
N13-H10N	0.900	2.753	144.09	3.521	S1
N21-H12N	0.900	2.646	155.30	3.484	S1
N22-H13N	0.900	2.275	161.18	3.141	S1
N22-H14N	0.900	2.307	173.34	3.203	S5
N23-H15N	0.890	1.944	168.38	2.822	N21 [x-1/2, -y, z]
N23-H16N	0.890	2.327	155.90	3.161	S6 [x, y-1, z]
N23-H17N	0.890	2.374	170.16	3.255	S2 [x, y-1, z]