Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Germylene Stabilized Group 12 Metal Complexes and their Reactivity with Chalcogens

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CONTENTS

Table S1. Crystal data and structure refinement for compounds 2, 3, 5, and 6

	2	**3**	**5**	**6**
Empirical formula	$C_{36}H_{60}Ge_2ZnCl_2N_4$	$C_{36}H_{60}Ge_2CdI_2N_4$	$C_{36}H_{60}Ge_2I_4N_4Zn_2$	$C_{38}H_{62}Cd_2Cl_8Ge_2N_4$
Formula weight	830.39	1060.31	1332.00	1228.56
Temperature, K	200(2)	150(2)	304(2)	302.11
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	*Pbca*	*Pbca*	$P2_1/n$
Unit cell dimensions	a = 12.144(4) Å b = 24.530(8) Å c = 13.845(4) Å β = 96.653(7)°	a = 17.8395(18) Å b = 19.3485(19) Å c = 24.563(2) Å	a = 18.971(3) Å b = 13.241(19) Å c = 21.886(4) Å	a = 12.595(9) Å b = 14.996(1) Å c = 14.499(10) Å β = 106.891(2)°
Volume, Å^3	4097(2)	8478.5(14)	5497.6(15)	2620.5(3)
Z	4	8	4	2
Density (calculated), Mg/m^3	1.346	1.661	1.609	1.557
Absorption coefficient, mm^{-1}	2.197	3.390	4.215	2.373
F(000)	1728.0	4176.0	2559	1228.1
Crystal size, mm^3	0.470 x 0.260 x 0.130	0.510 x 0.260 x 0.140	0.35 x 0.26 x 0.16	0.28 x 0.21 x 0.18
θ range for data collection, °	4.08 to 25.03	1.66 to 25.00	5.282 to 49.962	4 to 50
Limiting indices	-13 ≤ h ≤ 14, -29 ≤ k ≤ 29, -12 ≤ l ≤ 16	-19 ≤ h ≤ 21, -23 ≤ k ≤ 23, -23 ≤ l ≤ 29	-22 ≤ h ≤ 22, -15 ≤ k ≤ 15, -25 ≤ l ≤ 25	-16 ≤ h ≤ 16, -20 ≤ k ≤ 20, -19 ≤ l ≤ 19
Reflections collected	21214	42740	37727	46679
Independent reflections	7170 [R_{int} = 0.0836]	7462 [R_{int} = 0.0570]	4834 [R_{int} = 0.1657]	3915 [R_{int} = 0.0779]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7170 / 0 / 424	7462 / 22 / 412	4834 / 0 / 224	3915 / 0 / 260
Goodness-of-fit on F^2	1.155	1.033	1.046	1.032
Final R indices [I>2σ(I)]	R_1 = 0.0994, wR_2 = 0.2577	R_1 = 0.0544, wR_2 = 0.1411	R_1 = 0.0592 wR_2 = 0.1517	R_1 = 0.0385, wR_2 = 0.0837

R indices (all data)	$R_1 = 0.1289$, $wR_2 = 0.2711$	$R_1 = 0.0755$, $wR_2 = 0.1530$	$R_1 = 0.0752$, $wR_2 = 0.1688$	$R_1 = 0.0543$, $wR_2 = 0.0880$
Largest diff. peak and hole, $eÅ^{-3}$	1.979 and -0.776	1.991 and -1.408	0.92 and -0.64	0.78 and -0.69

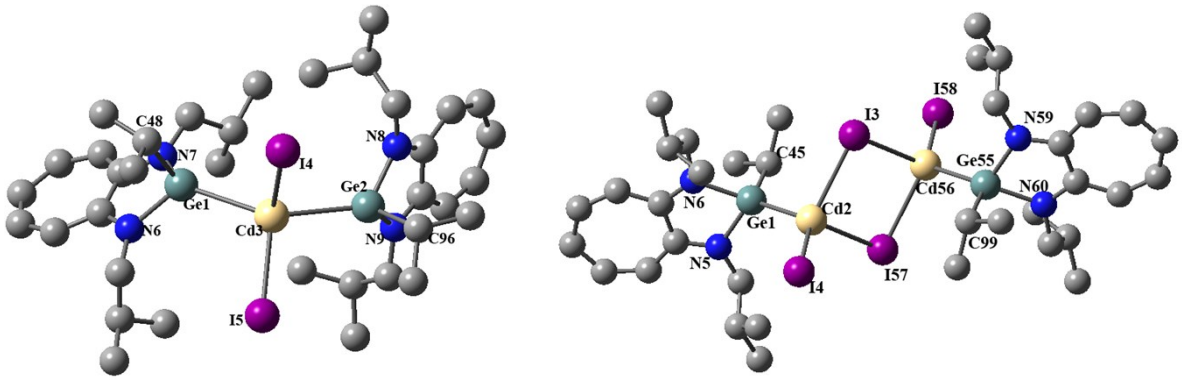
Table S2. Crystal data and structure refinement for compounds 7 and 9.

	7	**9**
Empirical formula	$C_{36}H_{60}Ge_2Cd_2I_4N_4$	$C_{36}H_{60}Cl_4Ge_2N_4Se_2Zn_2$
Formula weight	1426.52	1124.60
Temperature, K	100(2)	150(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	P-1
Unit cell dimensions	a = 9.1533(15) Å b = 26.486(5) Å c = 10.1617(17) Å β = 106.896(3)°	a = 10.268(2) Å b = 11.193(2) Å c = 12.837(3) Å α = 87.685(4)° β = 79.561(5)° γ = 75.846(5)°
Volume, Å^3	2357.2(7)	1406.9(5)
Z	2	1
Density (calculated), Mg/m^3	2.010	1.327
Absorption coefficient, mm^{-1}	4.800	3.408
F(000)	1352.0	564.0
Crystal size, mm^3	0.430 x 0.210 x 0.120	0.3 × 0.25 × 0.15
2θ range for data collection, °	1.54 to 25.00	1.88 to 25.00
Limiting indices	-10 ≤ h ≤ 9, -31 ≤ k ≤ 31, -8 ≤ l ≤ 12	-7 ≤ h ≤ 12, -13 ≤ k ≤ 13, -14 ≤ l ≤ 15
Reflections collected	12266	7145
Independent reflections	4139 [R_{int} = 0.0485]	4874 [R_{int} = 0.0645]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents

Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4146 / 0 / 223	4874 / 0 / 226
Goodness-of-fit on F^2	1.027	0.918
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0343$, $wR_2 = 0.0744$	$R_1 = 0.0807$, $wR_2 = 0.1692$
R indices (all data)	$R_1 = 0.0479$, $wR_2 = 0.0912$	$R_1 = 0.1328$, $wR_2 = 0.1871$
Largest diff. peak and hole, eÅ^{-3}	1.099 and -0.720	1.01 and -0.76

Computational details.

Theoretical calculations were performed using Gaussian 09 package.[S1] For geometry optimizations the coordinates obtained from single crystal X-ray diffraction studies on compounds **3** and **7** were used. The initial structures of compounds **3** and **7** were optimized using Hartree Fock (HF) level of theory utilizing LANL2DZ basis set for germanium, cadmium, and iodine atoms and 6-31+G** basis set for the rest of the atoms. The energy minimized geometries obtained were further optimized at Becke-3-parameter-Lee-Yang-Parr (B3LYP) level of theory using the aforementioned basis sets. The frequency calculations were also carried out on all the optimized geometries and the corresponding stationary minima were characterized. Natural bond orbital (NBO) analysis was performed using B3LYP theory level and split basis set used in the geometry optimizations.[S2] Natural population analysis (NPA) was performed by employing NBO 3.1 program incorporated in Gaussian program package. Gauss view and Chemcraft (http://www.chemcraftprog.com) were used for visualization and rendering.[S3] The optimized structures are shown in Figure S1 and a comparison of the optimized bond distances and bond angles with the corresponding experimental values is provided in Table S3.



(a) (b)

Figure S1. Optimized geometries of (a) compound 3 and (b) compound 7. Hydrogen atoms are not shown for clarity.

Table S3. Comparison of the important bond angles and lengths in compounds 3 and 7 obtained from experimental studies with the corresponding values calculated using DFT calculations.

Parameter labels used in theoretical studies	Corresponding parameter labels in the CIF file	Bond angles (°)/lengths (Å)	
		Calculated through DFT	Observed through CIF
Compound **3**			
Ge1-Cd3	Ge1-Cd1	2.846	2.622(1)
Ge2-Cd3	Ge2-Cd1	2.896	2.655(1)
Cd3-I4	Cd1-I1	2.884	2.824(8)
Cd3-I5	Cd1-I2	2.911	2.871(8)
Ge1-C48	Ge1-C16	2.041	2.006(1)
Ge2-C96	Ge2-C34	2.040	1.996(9)
Ge1-N6	Ge1-N1	1.973	1.912(8)
Ge1-N7	Ge1-N2	1.973	1.927(6)
Ge2-N8	Ge2-N3	1.971	1.913(7)
Ge2-N9	Ge2-N4	1.984	1.931(6)
Ge1-Cd3-I4	Ge1-Cd1-I1	103.96	107.45(3)
Ge2-Cd3-I5	Ge2-Cd1-I2	101.52	107.87(3)
Ge1-Cd3-Ge2	Ge1-Cd1-Ge2	132.47	126.08(3)
Ge1-Cd3-I5	Ge1-Cd1-I2	94.47	95.50(3)
Ge2-Cd3-I4	Ge2-Cd1-I1	106.87	112.13(3)
I4-Cd3-I5	I1-Cd1-I2	118.32	104.69(2)
C96-Ge2-Cd3	C34-Ge2-Cd1	110.07	114.20(3)
C48-Ge1-Cd3	C16-Ge1-Cd1	114.60	119.90(3)
N6-Ge1-N7	N1-Ge1-N2	80.62	82.10(3)
N8-Ge2-N9	N3-Ge2-N4	80.26	81.70(3)

Compound **7**			
Ge1-Cd2	Ge1-Cd1	2.791	2.585(9)
Cd2-I3	Cd1-I2	3.032	2.703(7)
Cd2-I57	Cd1-I1	3.069	2.869(7)
Cd2-I4	Cd1-I1*	2.802	2.933(7)
Ge1-C45	Ge1-C16	2.030	1.988(6)
Ge1-N5	Ge1-N1	1.957	1.913(5)
Ge1-N6	Ge1-N2	1.958	1.910(5)
N5-Ge1-N6	N2-Ge1-N1	81.41	82.30(2)
C45-Ge1-Cd2	C16-Ge1-Cd1	119.82	117.46(2)
Ge1-Cd2-I57	Ge1-Cd1-I2	96.36	133.29(3)
Ge1-Cd2-I3	Ge1-Cd1-I1	104.58	108.23(3)
I57-Cd2-I3	I2-Cd1-I1	94.59	105.83(2)
Ge1-Cd2-I4	Ge1-Cd1-I1*	127.28	95.64(2)
I4-Cd2-I57	I1-Cd1-I1*	115.34	99.61(2)
Cd2-I3-Cd56	Cd1-I1-Cd1*	85.41	80.39(2)

*Symmetry transformation used to generate the equivalent atoms: -x, -y, -z+1.

Table S4. Wiberg bond index (WBI) of Ge-Cd and Cd-I bonds in compounds 3 and 7.

Compound	Bond type	WBI
Compound **3**	Ge1/2-Cd3	0.51
	Cd3-I4	0.52
	Cd3-I5	0.55
Compound **7**	Ge1/55-Cd2/56	0.54
	Cd2/56-I4/58	0.71
	Cd2/56-I3/57	0.39
	Cd2/56-I57/3	0.36

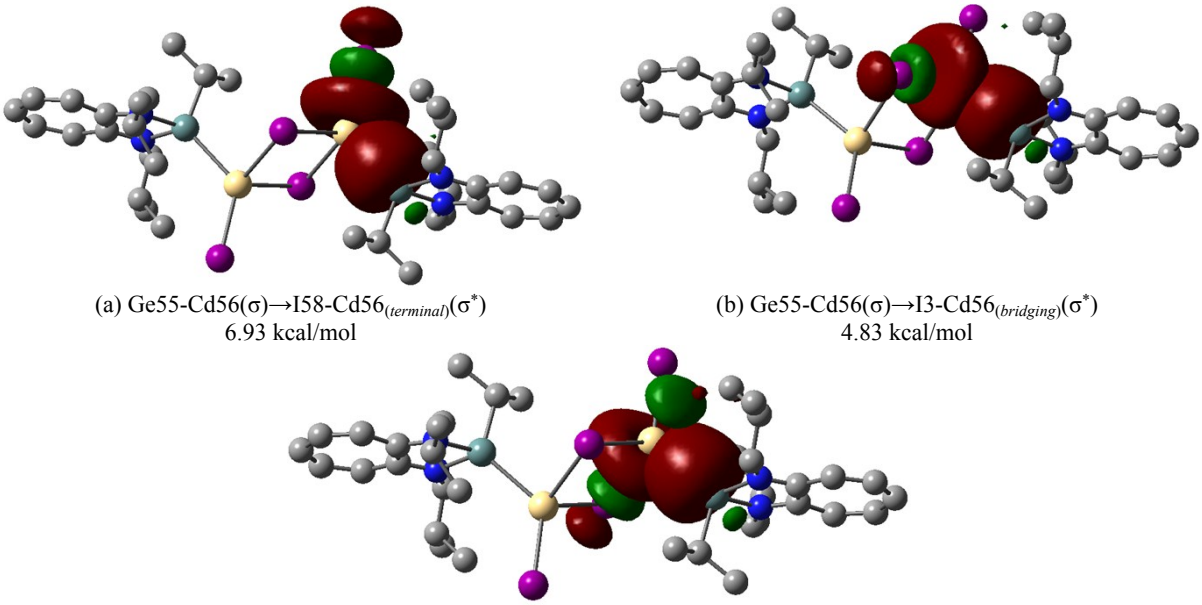


Figure S2. NBO diagrams of compound 7. Donor-acceptor interactions between Ge55-Cd56 bonding orbital and terminal and bridging I58/3/57-Cd56 antibonding orbitals are shown. Hydrogen atoms are omitted for clarity.

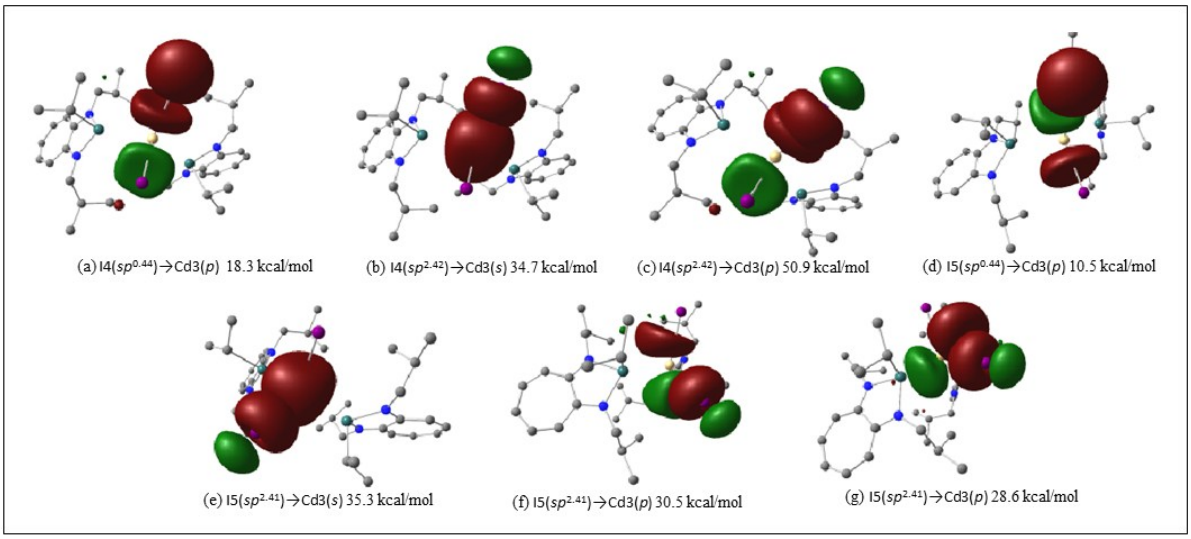
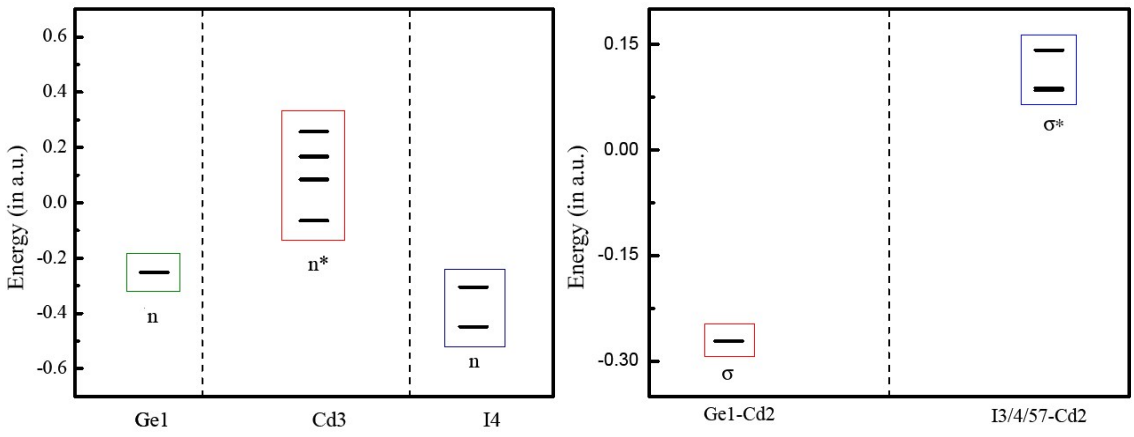


Figure S3. NBO diagrams of compound 3. Donor-acceptor interactions between I4/5→Cd3 atoms are shown with stabilization energies. Interaction threshold was chosen as 10 kcal/mol. Hydrogen atoms are omitted for clarity.

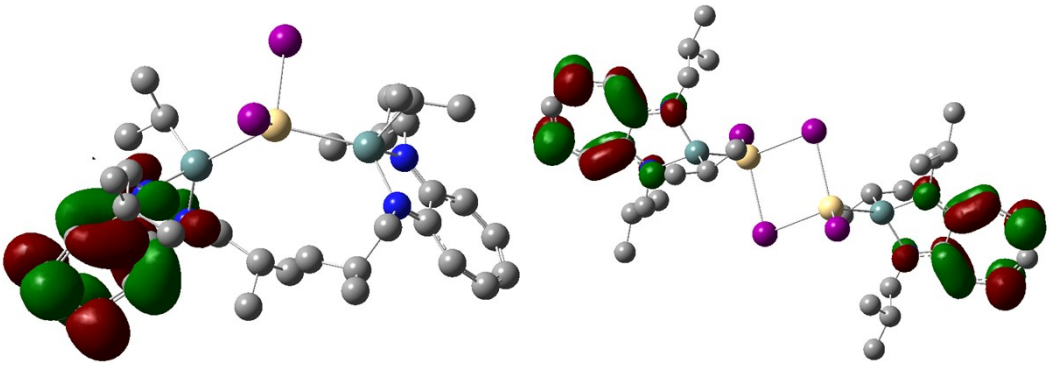


(a) (b)

Figure S4. Energy level diagrams for the donor-acceptor interactions in (a) compound 3 and (b) compound 7. Same diagrams for the donor-acceptor interactions between (a) Ge2→Cd3 and I5→Cd3 in compound **3**, and (b) Ge55-Cd56→I58/3/57-Cd56 in compound **7** can also be drawn.

Table S5. NPA charges on germanium, cadmium, and iodine atoms in compounds 3 and 7.

Compound 3	NPA charges (a.u.)	Compound 7	NPA charges (a.u.)
Ge1/Ge2	1.21	Ge1/Ge55	1.20
Cd3	0.51	Cd2 /Cd56	0.62
I4/I5	-0.57	I3/I57	-0.48
		I4/I58	-0.53



(a) (b)

Figure S5. The LUMOs of (a) compound 3 and (b) compound 7. The isosurface value is 0.032 a.u.

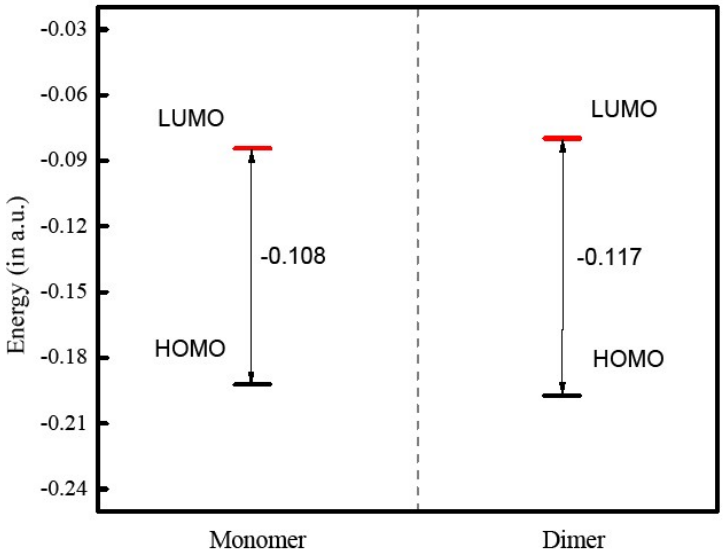


Figure S6. Energy level diagram that shows the HOMO and LUMO energies of compounds 3 (Monomer) and 7 (Dimer).

Coordinates for the optimized geometries of:

Compound 3

Ge	-2.6940410	-0.5740520	0.3220450
Ge	2.3686060	0.1683400	-0.8744630
Cd	-0.0196150	-1.3504800	-0.2632120
I	0.6634840	-3.1586800	1.8775690
I	-0.6742590	-2.4763000	-2.8662090
N	-3.2874650	0.6308690	1.7670140
N	-3.7384970	0.7164960	-0.7440130
N	4.0046590	0.1232400	0.2247100
N	2.7988530	2.1045670	-0.8336780
C	-4.1436720	1.6027720	1.4116220
C	-4.7111820	2.4832920	2.3694600
H	-4.3791340	2.3107770	3.3851340
C	-5.6237840	3.5279110	2.2493470
H	-5.8607070	4.0226660	3.1896220
C	-6.2832370	4.0243270	1.1252130
H	-6.9668920	4.8545980	1.2758370
C	-6.1527140	3.5318450	-0.1736970
H	-6.7676060	4.0230140	-0.9258140
C	-5.3559060	2.5052570	-0.6718100
H	-5.4687370	2.3440120	-1.7359600
C	-4.4255570	1.6344030	-0.0453250

C	-2.8974090	0.3776110	3.1597640
H	-3.7955460	0.3666670	3.7924090
H	-2.4825080	-0.6354420	3.1998310
C	-3.9289750	0.5012760	-2.1863460
H	-5.0045890	0.4260970	-2.3999180
H	-3.4952780	-0.4755390	-2.4271680
C	-1.8482590	1.3455440	3.7586760
H	-2.2304510	2.3710690	3.6701830
C	-3.2872460	1.5491520	-3.1275460
H	-3.6798150	2.5412970	-2.8692080
C	-1.6715660	1.0279010	5.2522230
H	-2.6154300	1.1206380	5.8025140
H	-0.9486800	1.7105620	5.7112790
H	-1.2983590	0.0064180	5.3941300
C	-0.5073310	1.2752980	3.0166870
H	-0.0732520	0.2707340	3.0799530
H	0.2096810	1.9787850	3.4539640
H	-0.6195030	1.5287630	1.9579420
C	-3.6983630	1.2332520	-4.5747160
H	-3.2769520	1.9702670	-5.2667540
H	-4.7878230	1.2431970	-4.6991530
H	-3.3321540	0.2452840	-4.8774560
C	-1.7607940	1.5921380	-2.9855500

H	-1.4647930	1.8275030	-1.9580610
H	-1.3402790	2.3610120	-3.6439930
H	-1.3155260	0.6291930	-3.2574180
C	-4.0215450	-2.1207550	0.4385200
H	-3.8603080	-2.6475340	-0.5133930
C	-5.4919920	-1.6935480	0.5253670
H	-6.1464750	-2.5760470	0.5495890
H	-5.8030310	-1.0807430	-0.3267890
H	-5.6925900	-1.1203280	1.4392150
C	-3.6508770	-3.0900990	1.5760010
H	-3.8228400	-2.6381600	2.5613650
H	-2.6060820	-3.4130840	1.5350450
H	-4.2769110	-3.9911270	1.5256200
C	4.7493760	1.2391480	0.1788930
C	6.1127600	1.2390320	0.5699720
H	6.5018960	0.2553620	0.8026520
C	7.0480040	2.2620330	0.6880760
H	8.0368290	1.9318850	1.0010470
C	6.9059730	3.6343070	0.4793330
H	7.7732580	4.2593110	0.6708510
C	5.7449070	4.2707760	0.0426540
H	5.8095820	5.3535880	-0.0484800
C	4.5066650	3.7432960	-0.3166770

H	3.7905680	4.4937890	-0.6234330
C	4.0159430	2.4137430	-0.3527310
C	4.4403180	-1.1049670	0.9082590
H	5.3520870	-1.4975610	0.4336190
H	3.6580050	-1.8519000	0.7429860
C	1.8898760	3.0812960	-1.4374780
H	1.3917000	2.5826760	-2.2781970
H	2.4533260	3.9126050	-1.8766520
C	4.6663430	-0.9823350	2.4375950
H	5.5435900	-0.3481790	2.6153210
C	0.7875680	3.6262060	-0.4942850
H	0.1564140	2.7700030	-0.2186190
C	4.9784480	-2.3808010	2.9958330
H	5.2122220	-2.3242620	4.0644740
H	5.8393540	-2.8354910	2.4906130
H	4.1193410	-3.0498220	2.8746100
C	3.4751360	-0.3427110	3.1638390
H	3.2732530	0.6685630	2.7952610
H	3.6852400	-0.2699430	4.2370590
H	2.5692750	-0.9437750	3.0367890
C	-0.0779200	4.6375190	-1.2628160
H	0.5079590	5.5250940	-1.5337950
H	-0.9206100	4.9732200	-0.6491770

H	-0.4853280	4.2097100	-2.1841260
C	1.3208210	4.2448730	0.8053610
H	1.9616690	3.5513080	1.3570620
H	0.4858460	4.5176430	1.4599260
H	1.8932920	5.1594770	0.6099970
C	3.0867060	-0.3639600	-2.7086730
H	2.1991330	-0.3202310	-3.3558240
C	3.5478280	-1.8332080	-2.6696730
H	3.8125470	-2.1759840	-3.6786180
H	2.7661620	-2.5066460	-2.3026160
H	4.4378240	-1.9599210	-2.0405020
C	4.1735520	0.5484200	-3.2894000
H	5.0772740	0.5525380	-2.6675820
H	3.8388870	1.5859370	-3.3948080
H	4.4743240	0.1984960	-4.2869700

Compound 7

Ge	-3.8170080	-0.0512940	-0.7640180
Cd	-1.7458400	0.2450080	1.0837310
I	0.1513900	2.2273690	-0.2072530
I	-1.9800540	0.6013460	3.8540520
N	-5.2239800	-1.3635740	-0.4079740
N	-5.3576930	1.1561540	-0.7948160
C	-6.4842040	-0.9021240	-0.4984630
C	-7.5991180	-1.7720680	-0.4218620
H	-7.3406010	-2.8154930	-0.2967300
C	-8.9681570	-1.5353340	-0.4757730
H	-9.5790070	-2.4310090	-0.3809740
C	-9.6701070	-0.3420650	-0.6314590
H	-10.7542960	-0.4005960	-0.6340150
C	-9.0999130	0.9176490	-0.7967020
H	-9.8027020	1.7390980	-0.9218850
C	-7.7634810	1.3013020	-0.8357130
H	-7.6185080	2.3623430	-0.9921610
C	-6.5626730	0.5618890	-0.7109750
C	-4.8999390	-2.7864850	-0.2340000
H	-3.8416160	-2.9085090	-0.4912230
H	-5.4621100	-3.3792120	-0.9685650
C	-5.1908670	2.5995600	-1.0117220

H	-5.8272270	2.9171140	-1.8487060
H	-4.1581070	2.7580440	-1.3401900
C	-5.1204820	-3.3645690	1.1840970
H	-6.1731460	-3.2170560	1.4580340
C	-5.4474390	3.5040750	0.2170730
H	-6.4628190	3.3081180	0.5851870
C	-4.8424090	-4.8750370	1.1506350
H	-3.8006280	-5.0754290	0.8743420
H	-5.4864200	-5.3937440	0.4310680
H	-5.0139650	-5.3208360	2.1351850
C	-4.2578000	-2.6634980	2.2387680
H	-4.4479460	-3.0800380	3.2328930
H	-4.4639260	-1.5911250	2.2923340
H	-3.1904150	-2.7955340	2.0278320
C	-5.3741490	4.9733520	-0.2255530
H	-5.5726450	5.6414070	0.6180620
H	-6.1032270	5.2004890	-1.0118840
H	-4.3775510	5.2176760	-0.6119810
C	-4.4684390	3.2194520	1.3616810
H	-3.4329430	3.4036490	1.0511370
H	-4.5385790	2.1879580	1.7169380
H	-4.6733480	3.8706020	2.2171440
C	-3.3852170	-0.3605930	-2.7234560

H	-2.6433470	-1.1709150	-2.6929630
C	-4.5825450	-0.8140540	-3.5661040
H	-5.3724930	-0.0536260	-3.5857530
H	-5.0255340	-1.7444680	-3.1974000
H	-4.2742650	-0.9864900	-4.6053580
C	-2.7018600	0.8768880	-3.3323480
H	-2.3222590	0.6462560	-4.3347590
H	-1.8504110	1.2253710	-2.7396930
H	-3.4057550	1.7117100	-3.4375770
Ge	3.8169720	0.0512900	0.7640190
Cd	1.7458550	-0.2450270	-1.0837860
I	-0.1514020	-2.2273870	0.2071640
I	1.9801330	-0.6013640	-3.8541010
N	5.2239390	1.3635880	0.4080170
N	5.3576710	-1.1561400	0.7948590
C	6.4841650	0.9021520	0.4985450
C	7.5990690	1.7721130	0.4219890
H	7.3405410	2.8155340	0.2968510
C	8.9681090	1.5353990	0.4759540
H	9.5789500	2.4310820	0.3811800
C	9.6700700	0.3421400	0.6316670
H	10.7542580	0.4006870	0.6342660
C	9.0998880	-0.9175830	0.7968870

H	9.8026840	-1.7390220	0.9220970
C	7.7634610	-1.3012550	0.8358450
H	7.6184960	-2.3622980	0.9922870
C	6.5626470	-0.5618600	0.7110590
C	4.8998880	2.7864960	0.2340380
H	3.8415560	2.9085090	0.4912300
H	5.4620320	3.3792240	0.9686220
C	5.1908570	-2.5995490	1.0117610
H	5.8271860	-2.9170890	1.8487740
H	4.1580860	-2.7580500	1.3401870
C	5.1204690	3.3645900	-1.1840490
H	6.1731430	3.2170900	-1.4579550
C	5.4475000	-3.5040680	-0.2170180
H	6.4628900	-3.3080880	-0.5850930
C	4.8423820	4.8750550	-1.1505860
H	3.8005900	5.0754360	-0.8743260
H	5.4863640	5.3937620	-0.4309930
H	5.0139670	5.3208630	-2.1351260
C	4.2578270	2.6635190	-2.2387530
H	4.4480020	3.0800690	-3.2328690
H	4.4639640	1.5911490	-2.2923200
H	3.1904340	2.7955450	-2.0278510
C	5.3742320	-4.9733430	0.2256160

H	5.5727790	-5.6413990	-0.6179860
H	6.1032840	-5.2004540	1.0119790
H	4.3776240	-5.2176900	0.6120060
C	4.4685390	-3.2194820	-1.3616680
H	3.4330360	-3.4037020	-1.0511650
H	4.5386670	-2.1879900	-1.7169340
H	4.6734990	-3.8706350	-2.2171170
C	3.3851190	0.3605760	2.7234440
H	2.6432180	1.1708700	2.6929310
C	4.5824070	0.8140840	3.5661230
H	5.3723830	0.0536850	3.5857950
H	5.0253710	1.7445140	3.1974310
H	4.2740920	0.9865100	4.6053690
C	2.7017940	-0.8769300	3.3323190
H	2.3221580	-0.6463110	4.3347200
H	1.8503740	-1.2254470	2.7396440
H	3.4057190	-1.7117250	3.4375670

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