Conductance of Single-Cobalt Chalcogenide Cluster Junctions

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Supplementary Information

I. Synthetic Details

General Synthesis Remarks: All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. All reagents were used as received from *Aldrich* except $Co_2(CO)_8$, Te, Se, S and triethylphosphine which were purchased from *Strem* and were used as received unless otherwise specified. Anhydrous and anaerobic solvents were obtained from a Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst (Glass Contour, Irvine, CA). Synthesis of **1**, and **4**-**8** were performed according to published results.[1] ^{1}H NMR (300MHz) and ^{13}C NMR (75MHz) spectra were recorded on a Bruker DRX-300 spectrometer at room temperature. Absorption spectra were taken on an Agilent Technologies 8453 UV/vis spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 400 spectrometer using a PIKE ATR attachment (w). X-ray powder diffractions patterns were recorded on a INEL X-ray diffractometer with Cu Kα radiation (λ = 1.54056 A). Elemental analyses were carried out by the Analytische Laboratorien in Lindlar, Germany.

$Co_6Se_8(PEt_3)_6$ (2)

Elemental Se (0.993 g, 12.6 mmol) and triethylphosphine (1.48 g, 1.85 mL, 12.6 mmol) were combined in toluene (25mL) and allowed to stir at room temperature until all Se was dissolved (~30 min). Dicobalt octacarbonyl (1.00 g, 2.92 mmol) was then added to the yellow solution of freshly prepared triethylphosphine selenide; rapid evolution of CO was observed and the reaction turned deep red. The mixture was stirred at room temperature for 1 hour and then heated to reflux for 16 hours. The resulting dark

red/black mixture was cooled to room temperature, Schlenk filtered and concentrated to 10 mL. The concentrated solution was then cooled to -20 ºC overnight to afford deep red needles. The mother liquor was decanted and crystals were washed with cold pentane (3 x 5mL). The material was then dried under vacuum to yield **2** (65% yield).

^{1}H NMR (399.95 MHz, [d_8-Toluene], 298 K): δ = 1.32, 1.30, 1.28, 1.26 (q, 36H, $^{3}J_{HH}$ = 6.0 Hz P(C**H**$_2$CH$_3$)$_3$), 0.87, 0.83, 0.80 (t, 54H, $^{3}J_{HH}$ = 10.0 Hz, P(CH$_2$C**H**$_3$)$_3$

λ_{max} (Ext. Coeff): 371nm (25070), 444 nm (18867), 507 nm (9789), See Figure S-1.

^{31}P NMR (100.61 MHz, d_8-Toluene, 298 K): δ = 153.5

IR: Sp^3 C-H stretches observed for coordinated PEt_3.

$Co_6S_8(PEt_3)_6$ (3)

Elemental S (0.420, 13.0 mmol) and triethylphosphine (1.53 g, 1.91 mL, 13.0 mmol) were combined in toluene (25 mL) and allowed to stir until S was completely dissolved (~20 min). Dicobalt octacarbonyl (1.03 g, 3.02 mmol) was then added to the yellow solution of freshly prepared triethylphosphine sulfide, rapid evolution of CO was observed and the reaction turns deep red/orange. The reaction mixture was allowed to stir at room temperature for 1.5 hours. The reaction mixture was then heated to 100 º C for 5 hours. The resulting dark orange/black mixture was cooled to room temperature, Schlenk filtered, and excess toluene was concentrated to ~2 mL. Diethyl ether (10 mL) was then added to mixture. The mixture was warmed slightly to ensure all of the remaining solid was dissolved and was then cooled to-20 ºC for one week to afford deep red/black needles. The mother liquor was decanted and crystals were washed with cold pentane (3 x 5mL). The material was then dried under vacuum to yield **3** (53 % yield).

^{1}H NMR (399.95 MHz, [d_6- Benzene], 298 K): δ = 1.28, 1.26, 1.22, 1.19 (q, 36H, $^{3}J_{HH}$ = 6.0 Hz P(C**H**$_2$CH$_3$)$_3$), 0.92, 0.89, 0.87 (t, 54H, $^{3}J_{HH}$ = 10.0 Hz, P(CH$_2$C**H**$_3$)$_3$.

λ_{max} (Ext. Coeff): 342 nm (6427), 412 nm (4390), 480 nm (2159), See figure S-1.

^{31}P NMR (100.61 MHz, d_6- Benzene, 298 K): δ = 140.6

IR: Sp^3 C-H stretches observed for coordinated PEt_3.

XRD: Powder pattern of **3**. 2-Theta values: 7.545, 9.459, 10.416, 10.938, 11.315, 12.968, 15.288, 18.043, 18.507, 19.754, 22.886, 26.975, 28.222, 30.484, 33.732, 34.66, 40.199, 44.462, 49.247. 53.568. See Figure S-2.

$Co_6Te_8(PEt_3)_6^{+1}$

$Co_6Te_8(PEt_3)_6$ (50 mg, 0.024 mmol) was suspended in acetonitrile (15 mL). Ferrocenium tetrafluoroborate (7 mg, 0.024 mmol) was added at one time as a solid. The reaction mixture was allowed to stir at room temperature for 2 hours before being filtered and the solvent removed under vacuum. The solid black product was washed with hexanes (3 x 3 mL) and dried under vacuum to yield $Co_6Te_8(PEt_3)_6^{+1}$, a deep red/black powder (89 % yield). Elem. Anal. Calc. for $Co_6Te_8(PEt_3)_6^{+1}$ (156.3): C, 19.93; H, 4.19; P, 8.57; Co, 16.30; Te, 47.06; F, 3.50. Found: C, 19.74; H, 4.08; P, 8.44; Co, 16.45; Te, 47.30; F, 3.41.

II. UV-Vis Absorption Spectroscopy

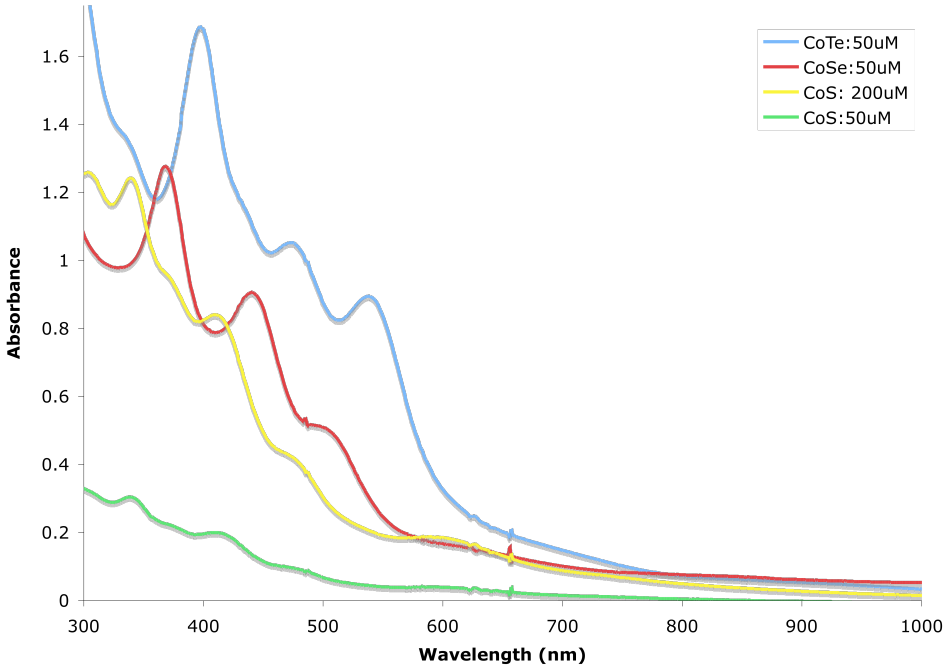

Figure S-1. UV spectra were taken in toluene with the following concentrations: **1** (Blue 50 μM), **2** (Red 50 μM) and **3** (Yellow 200 μM, Green 50 μM). E_g was calculated with the following absorption onset values **1** (642 nm), **2** (574 nm) and **3** (533 nm).

III. Powder X-Ray Diffraction

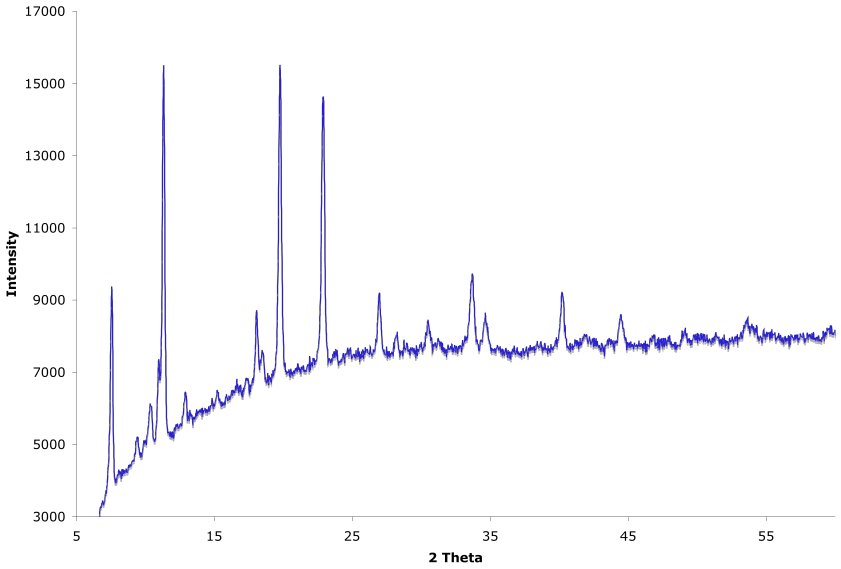

Figure S-2. Powder X-Ray Diffraction Pattern of $Co_6S_8(PEt_3)_6$.

IV. Conductance Measurements.

General Conductance Remarks: The series of conductance measurements performed on molecules **1-8** were performed in a home-built modified scanning tunneling microscope (STM) that has been previously described.[2] Briefly, a gold tip (Alfa Aesar, 99.999%) is brought in and out of contact with a gold-on-mica substrate in a ~1mM (**4-6**) or 100μM (**1-3, 7-8**) solution in 1,2,4-trichlorobenzene (Aldrich, anhydrous, 99+%). A gold point-contact is first formed and as it is broken, a molecule can be trapped between the broken ends to form a single molecular junction. The junction conductance (current/voltage) is measured at a constant applied bias of 25-100 mV as a function of the sample displacement (while the tip is held fixed), resulting in the conductance trace. Typical conductance traces show steps at integer multiples of the quantum of conductance, $G_0 = 2e^2/h \approx 77\mu S$, and a step at a molecule dependent value below G_0. For the displacement rates used, the whole conductance traces shown span less than 100ms. Since successive conductance traces are not identical, and since molecules are not trapped in every trace, thousands of conductance traces are collected. The data points of all the measured traces are compiled into a histogram of conductance for a statistical analysis, using linear conductance bins (example inset of Figure S-3) and logarithm bins (example in Figure S-3). Peaks in the linear binned histograms result when a significant fraction of all measured traces show plateaus at a narrow conductance range.

Additional Conductance Experiments: To further demonstrate that gold point contacts were being made between the chalcogenides, compounds **7** and **8** were examined. Increased alkyl bulk resulted in no conductance and no loss of the G_0 peak (Figure S-3.)

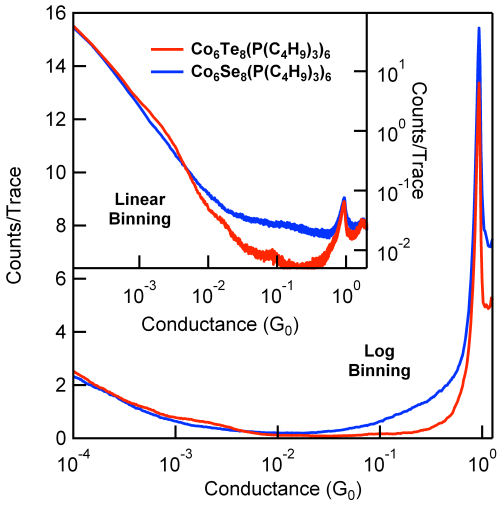

Figure S-3. Logarithmically binned conductance histograms for compounds **7** (in red) and **8** (in blue). Inset: Same histograms generated using linear bins.

Additional controls were performed taking conductance measurements of $SePEt_3$ and $Co_2(CO)_8$ to ensure conductance was in fact being measured through the cluster and not any unreacted starting materials, as well as the possibility of isolated Au-X-Au (X= chalcogenide) junction formation (Figure S-4).

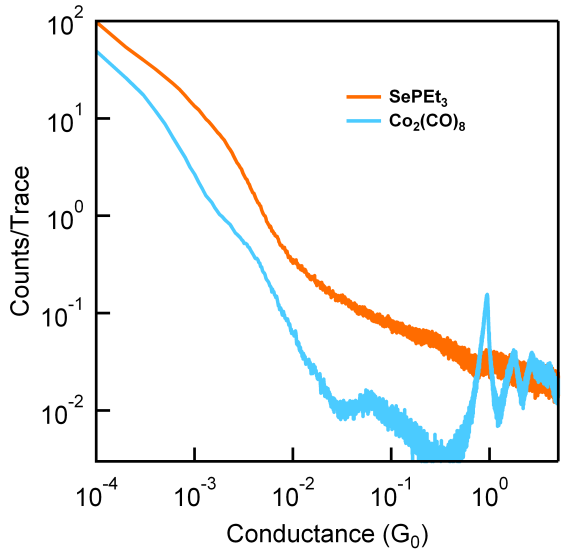

Figure S-4. Conductance histograms for the two starting compounds $SePEt_3$ (orange) and $Co_2(CO)_8$ (blue) generated using linear bins.

V. Electrochemistry

The electrochemistry of **3** has been previously reported.[3] A solution of $Co_6Te_8(PEt_3)_6^{+1}$ in dichloromethane containing 0.1 M of supporting electrolyte, tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was used in a single cell with a CH Instruments Electrochemical analyzer potentiostat assembly for cyclic voltammetry measurements. Similarly, a solution of **2** in dimethylformamide containing 0.1 M $TBAPF_6$ was used for cylic voltammetry measurements in the same single cell setup. The measurements were carried out with a glassy carbon working electrode, a platinum wire counter electrode and an Ag^+/AgCl reference electrode. The potentials were measured against a Ag^+/AgCl reference electrode and each measurement was calibrated using ferrocene/ferrocenium (Fer) redox system.[4] HOMO energy levels were calculated from cyclic voltammetry data based on calculations described by Micaroni et. al.[5] The +1/0 reduction potential and 0/+1 oxidation potential in the CV for **1** and **2**, respectively, were irreversible due to lack of solubility. As a result, HOMO levels are estimated as a range using the peak potential to obtain one HOMO value and a second potential, estimated by adding half of the largest potential gap of all the reversible redox couples in that particular CV, to obtain the other HOMO value. The voltammagrams from **1** and **2** (Figures S5-S6) can be seen below as well as the HOMO values (Table S-1).

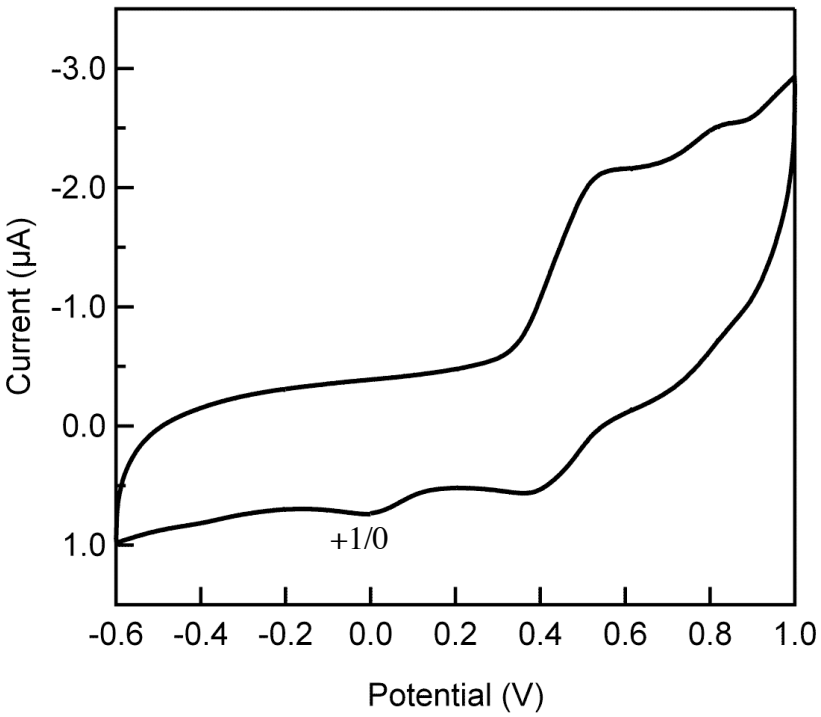

Figure S-4. CV trace of $Co_6Te_8(PEt_3)_6^{+1}$ in 0.1 M $TBAPF_6$ in dichloromethane.

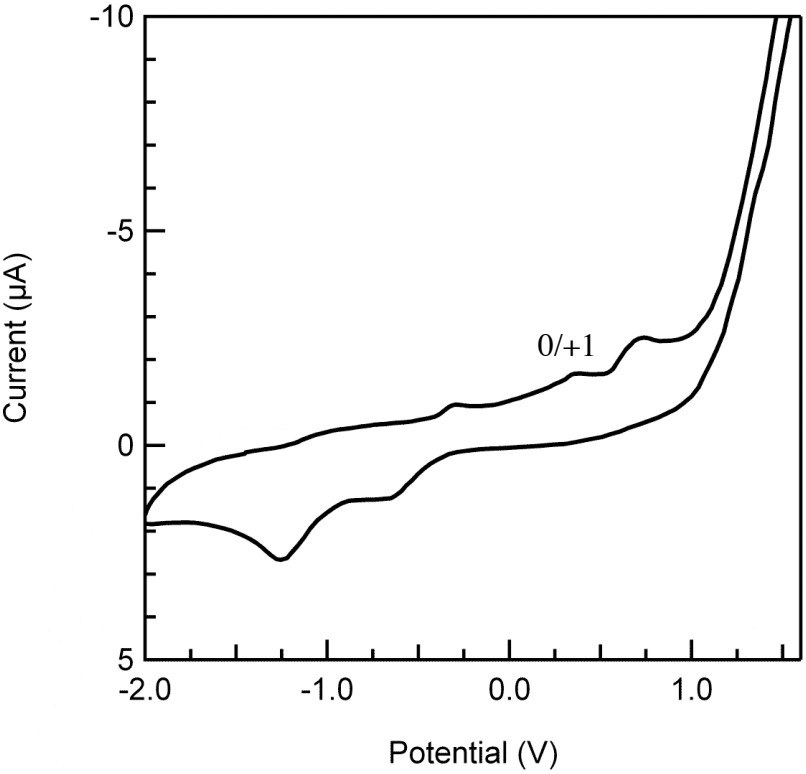

Figure S-5. CV trace of $Co_6Se_8(PEt_3)_6$ in 0.1 M $TBAPF_6$ in dimethylformamide.

Table S-1: HOMO and E_g values determined from CV and UV-Vis measurements, respectively, and from DFT based calculations for **1**-**3**.

Cluster	Homo[(a)](eV)	DFT: Homo (eV)	E_g[(b)] (eV)	DFT: E_g (eV)
1	- 4.36 to -4.44	- 4.0	1.92	2.5
2	- 4.54 to -4.67	- 4.3	2.15	2.9
3	- 4.79	- 4.6	2.31	3.1

(a) HOMO energy levels were calculated from cyclic voltammetry data based on calculations described by Micaroni *et. al.*[5] The +1/0 reduction potential and 0/+1 oxidation potential in the CV for **1** and **2**, respectively, were irreversible due to lack of solubility. As a result, HOMO levels are estimated as a range using the peak potential to obtain one HOMO value and a second potential, estimated by adding half of the largest potential difference of all the reversible redox couples in that particular CV, to obtain the other HOMO value. (b) Estimated from optical absorption. E_g are slightly variable as the absorption onset (λ') is difficult to obtain from the absorbance data of the clusters (Figure S-1).

VI. DFT Calculations:

Summary for Compound 1: $Co_6Te_8(PMe_3)_6$

All dft calculations were performed using Jaguar, version 7.0, Schrodinger, LLC, New York, NY, 2007

B3LYP, LCVP**/6-31G**

Final total energy = -3702.138365 hartree

HOMO energy: -0.14661 h

LUMO energy: -0.05608 h

Orbital energies (in hartrees):

-77.09120 -77.09116 -77.09112 -77.09110 -77.09107 -77.09105

-10.17427 -10.17416 -10.17408 -10.17403 -10.17400 -10.17383

-10.17372 -10.17371 -10.17370 -10.17358 -10.17349 -10.17342

-10.17265 -10.17258 -10.17252 -10.17248 -10.17241 -10.17240

-6.56816 -6.56806 -6.56804 -6.56803 -6.56801 -6.56801

-4.73006 -4.73004 -4.72997 -4.72995 -4.72993 -4.72993

-4.72993 -4.72992 -4.72992 -4.72991 -4.72990 -4.72990

-4.72696 -4.72684 -4.72684 -4.72683 -4.72682 -4.72681

-3.69209 -3.69189 -3.69186 -3.69152 -3.69129 -3.69080

-2.38891 -2.38884 -2.38851 -2.38826 -2.38825 -2.38817

-2.38231 -2.38202 -2.38181 -2.38165 -2.38149 -2.38131

-2.38124 -2.38117 -2.38112 -2.38072 -2.38044 -2.38000

-0.76435 -0.76413 -0.76406 -0.76396 -0.76393 -0.76387

-0.68828 -0.68820 -0.68815 -0.68811 -0.68803 -0.68802

-0.68728 -0.68721 -0.68715 -0.68710 -0.68695 -0.68694

-0.59308 -0.56332 -0.56268 -0.56242 -0.53912 -0.53909

-0.53857 -0.53644 -0.53632 -0.53546 -0.53532 -0.53505

-0.53314 -0.52077 -0.44095 -0.44086 -0.43914 -0.43856

-0.43844 -0.43758 -0.42317 -0.42306 -0.42296 -0.42293

-0.42291 -0.42264 -0.42258 -0.42248 -0.42240 -0.42233

-0.42181 -0.42151 -0.40054 -0.40038 -0.40016 -0.39951

-0.39940 -0.39933 -0.39853 -0.39831 -0.39816 -0.39807

-0.39744 -0.39739 -0.38248 -0.38236 -0.38230 -0.38219

-0.38212 -0.38202 -0.33174 -0.33163 -0.33159 -0.33149

-0.33143 -0.33134 -0.33073 -0.33062 -0.33056 -0.33046

-0.33040 -0.33027 -0.31815 -0.31805 -0.30331 -0.30115

-0.30088 -0.29982 -0.27377 -0.27252 -0.27149 -0.27137

-0.27106 -0.27094 -0.27093 -0.26756 -0.26722 -0.26260

-0.26086 -0.26058 -0.23913 -0.23912 -0.23846 -0.22907

-0.22902 -0.22774 -0.22272 -0.22255 -0.22191 -0.22045

-0.21992 -0.21898 -0.21878 -0.21632 -0.21612 -0.21504

-0.20969 -0.20925 -0.19066 -0.19030 -0.19002 -0.18782

-0.18781 -0.18744 -0.17491 -0.17412 -0.17370 -0.15881

-0.15052 -0.15007 -0.14661 -0.05608 -0.05578 -0.05533

-0.05116 -0.05073 -0.04140 -0.04097 -0.03923 -0.03495

-0.03451

final geometry:

angstroms

atom	x	y	z
Co1	-0.0101915779	-0.0303717714	0.0968237043
P2	-0.0059179740	-0.0116335455	2.2915253514
Co3	2.3477559527	0.0110830514	-2.0496389345
P4	4.5346971477	0.1553959367	-1.9386557858
Co5	0.0671482969	2.2219732866	-2.1375264535
P6	0.0406358522	4.4144174766	-2.0270344853
Te7	1.7905420735	-1.8143117077	-0.3204699080
Co8	0.1020754319	-2.3015501052	-2.1995454165
P9	0.1603611065	-4.4929622160	-2.3178662636
Te10	-1.7545168504	-1.8505647813	-0.4576834097
Co11	-2.1835820981	-0.0899589726	-2.2884869223
P12	-4.3700208386	-0.2327713081	-2.4085039174
Te13	-1.8332030347	1.7090807065	-0.4702621771
Te14	1.7873969133	1.7921831140	-0.2623062656

Co15	0.1718994396	-0.0482099627	-4.4340102815
P16	0.1578471278	-0.0624123077	-6.6281772748
Te17	1.9968099997	-1.7872337839	-3.8697958616
Te18	-1.6225131870	-1.8712956745	-4.0714740491
Te19	1.9184134560	1.7683967942	-3.8823553141
Te20	-1.6254824003	1.7379009621	-4.0134987973
C21	-5.1111135893	-1.9267027381	-2.3381764942
C22	-5.1697865410	0.4252114753	-3.9399087410
C23	-5.3548337749	0.6219350590	-1.0982856677
C24	5.2748417844	1.8493345016	-2.0173608554
C25	5.3409460402	-0.4982725874	-0.4089530812
C26	5.5144207959	-0.7016584196	-3.2512476875
C27	1.1008577771	1.2685977541	-7.4978773419
C28	-1.4864564753	0.0838556421	-7.4637179024
C29	0.8271502882	-1.5724760008	-7.4584193332
C30	1.6339363425	-0.1722903061	3.1330270457
C31	-0.9657609222	-1.3302907104	3.1615996694
C32	-0.6627369872	1.5071909692	3.1160136173
C33	-1.2528819222	-5.4191296320	-1.5677631366
C34	0.2035620581	-5.2466571295	-4.0074094780
C35	1.6008873372	-5.3466373035	-1.5337675726

C36	-1.3189175618	5.2948483782	-2.9184547597
C37	1.5243959283	5.3087361495	-2.6731063070
C38	-0.1093924428	5.1741032571	-0.3465366191
H39	-1.3690873084	0.0457753518	-8.5524893727
H40	-2.1331154489	-0.7341170331	-7.1381795225
H41	-1.9583816470	1.0270282216	-7.1798993699
H42	0.7214376438	-1.4962397721	-8.5463835852
H43	1.8808125134	-1.6971552860	-7.2000409871
H44	0.2849984231	-2.4509205546	-7.1003233549
H45	0.9972813372	1.1702692798	-8.5843054171
H46	0.7252887939	2.2450470662	-7.1826796874
H47	2.1565716865	1.2105159546	-7.2240361437
H48	-6.2527531354	0.2600111379	-3.9138586562
H49	-4.9636642391	1.4937283938	-4.0317425226
H50	-4.7453463515	-0.0769678102	-4.8125536559
H51	-6.2022471944	-1.8724584363	-2.4225598802
H52	-4.7119887903	-2.5332352163	-3.1541984151
H53	-4.8413300197	-2.4039414204	-1.3934620119
H54	-6.4269895560	0.4505363731	-1.2460071364
H55	-5.0572065557	0.2450593867	-0.1167960742
H56	-5.1485401423	1.6941396269	-1.1231776546

H57	-0.8658962135	-1.2284587577	4.2480614783
H58	-2.0197277388	-1.2629747391	2.8830247882
H59	-0.5985054771	-2.3116805690	2.8519489046
H60	-0.5598395257	1.4330099760	4.2043949485
H61	-0.1117332366	2.3795297350	2.7565240796
H62	-1.7147052742	1.6410196397	2.8553005835
H63	1.5135619247	-0.1294807006	4.2212856693
H64	2.0974587378	-1.1209258124	2.8536048871
H65	2.2898467406	0.6380543260	2.8068093372
H66	6.5869662143	-0.5275103521	-3.1096158441
H67	5.3106119705	-1.7742004258	-3.2219232695
H68	5.2109718580	-0.3285566603	-4.2323581769
H69	6.3661194516	1.7957203029	-1.9344194247
H70	5.0035339180	2.3223583221	-2.9636869346
H71	4.8768723207	2.4591423815	-1.2031964980
H72	6.4239978028	-0.3345611483	-0.4401329279
H73	4.9207545715	0.0073731739	0.4637728189
H74	5.1337846664	-1.5662227706	-0.3125296651
H75	0.2514371359	-6.3392137477	-3.9391574647
H76	-0.6912689129	-4.9544656079	-4.5611622976
H77	1.0774516619	-4.8764437409	-4.5481950187

H78	-1.1363815031	-6.4975726754	-1.7235893521
H79	-1.3043710946	-5.2069589511	-0.4976283707
H80	-2.1878487505	-5.0838665436	-2.0230360451
H81	1.5455042936	-6.4287553608	-1.6971621153
H82	2.5275706745	-4.9599097427	-1.9647622879
H83	1.6148096852	-5.1378400418	-0.4619599639
H84	-1.2479498423	6.3769622591	-2.7613402974
H85	-1.2617620416	5.0752013676	-3.9867121339
H86	-2.2838909120	4.9358484829	-2.5524948873
H87	1.4230661971	6.3890951736	-2.5200553478
H88	2.4170455588	4.9494159916	-2.1555538052
H89	1.6443706079	5.0989344845	-3.7380888456
H90	-0.1143734743	6.2674864208	-0.4182950155
H91	-1.0340976085	4.8350549928	0.1257111915
H92	0.7299926691	4.8532065735	0.2742813285

principal moments of inertia:

amu*angstrom^2: 15741.29261 16193.10707 16251.40193

g*cm^2: 2.61390281E-36 2.68892836E-36 2.69860844E-36

rotational constants:

cm^(-1): 0.00107092 0.00104104 0.00103730

GHz: 0.03210531 0.03120951 0.03109756

Summary for Compound 2: $Co_6Se_8(PMe_3)_6$

All dft calculations were performed using Jaguar, version 7.0, Schrodinger, LLC, New York, NY, 2007

B3LYP, LCVP**/6-31G**

Final total energy = -3711.624468 hartree

HOMO energy: -0.15816 h

LUMO energy: -0.05316 h

Orbital energies (in hartrees):

-77.09093 -77.09084 -77.09081 -77.09076 -77.09068 -77.09063

-10.17339 -10.17338 -10.17332 -10.17323 -10.17305 -10.17298

-10.17295 -10.17292 -10.17291 -10.17271 -10.17269 -10.17264

-10.17161 -10.17149 -10.17141 -10.17137 -10.17130 -10.17116

-6.56820 -6.56812 -6.56808 -6.56802 -6.56798 -6.56789

-4.73003 -4.73000 -4.72995 -4.72992 -4.72991 -4.72988

-4.72986 -4.72982 -4.72981 -4.72978 -4.72973 -4.72970

-4.72709 -4.72701 -4.72698 -4.72692 -4.72688 -4.72680

-3.70116 -3.70113 -3.70105 -3.70100 -3.70099 -3.70085

-2.39531 -2.39529 -2.39527 -2.39514 -2.39512 -2.39490

-2.39195 -2.39191 -2.39189 -2.39186 -2.39184 -2.39172

-2.39147 -2.39142 -2.39139 -2.39135 -2.39131 -2.39108

-0.76430 -0.76390 -0.76379 -0.76374 -0.76358 -0.76349

-0.68795 -0.68792 -0.68780 -0.68777 -0.68763 -0.68759

-0.68684 -0.68677 -0.68671 -0.68656 -0.68644 -0.68635

-0.64410 -0.61503 -0.61484 -0.61457 -0.59389 -0.59214

-0.59196 -0.58031 -0.53784 -0.53781 -0.53692 -0.53687

-0.53670 -0.53589 -0.43967 -0.43961 -0.43848 -0.43749

-0.43734 -0.43713 -0.42233 -0.42202 -0.42196 -0.42189

-0.42169 -0.42166 -0.42156 -0.42143 -0.42136 -0.42132

-0.42117 -0.42091 -0.40039 -0.40030 -0.39993 -0.39945

-0.39924 -0.39911 -0.39853 -0.39836 -0.39834 -0.39816

-0.39715 -0.39707 -0.38132 -0.38116 -0.38105 -0.38098

-0.38071 -0.38065 -0.33231 -0.33228 -0.33215 -0.33211

-0.33197 -0.33191 -0.33104 -0.33099 -0.33072 -0.33068

-0.33066 -0.33034 -0.32718 -0.32711 -0.31872 -0.30900

-0.30895 -0.30830 -0.28559 -0.28284 -0.28263 -0.28166

-0.28007 -0.27991 -0.27968 -0.27814 -0.27794 -0.27774

-0.27561 -0.27544 -0.25326 -0.25316 -0.25312 -0.23886

-0.23691 -0.23689 -0.23575 -0.23090 -0.23079 -0.22949

-0.22840 -0.22832 -0.22664 -0.22662 -0.22593 -0.22090

-0.21535 -0.21518 -0.19898 -0.19699 -0.19675 -0.19152

-0.19127 -0.18964 -0.18173 -0.18023 -0.18005 -0.17086

-0.16053 -0.16028 -0.15816 -0.05316 -0.05312 -0.05304

-0.04451 -0.04444 -0.03576 -0.03569 -0.03453 -0.03225

-0.03207

final geometry:

angstroms

atom	x	y	z
Co1	-0.0160463740	-0.0112772881	0.0184650420
P2	0.0027651706	0.0005235449	2.2013621562
Co3	2.0607685174	-0.0142303535	-2.1029817124
P4	4.2417728391	-0.0640352539	-2.2111398472
Co5	0.0296819889	2.1469512041	-1.9794410654
P6	0.0088350032	4.3287398928	-1.8861313182
Co7	-2.1170900966	0.1316282091	-2.0356515981
P8	-4.2968834051	0.1978905804	-1.9210857378
Co9	-0.0846724299	-2.0259233375	-2.1581229531
P10	-0.0456299912	-4.2077359836	-2.2393574426
Se11	1.7336710210	1.6119453305	-0.3469191986
Se12	1.6081260876	-1.7331375193	-0.4629981164
Se13	-1.7421698881	-1.6452913292	-0.4415043854
Se14	-1.6572231770	1.7471649716	-0.2847277789
Co15	-0.0416261656	0.1371007469	-4.1561101369

P16	-0.0543409810	0.1676402570	-6.3404042533
Se17	1.6882896880	1.7644222298	-3.6942879197
Se18	1.5968652894	-1.6256616186	-3.8571051969
Se19	-1.6668381522	1.8552164217	-3.6724213715
Se20	-1.7881617087	-1.4944492302	-3.7930938326
C21	1.6229681921	-4.9910408066	-2.1562957430
C22	-0.7452991853	-4.9850461634	-3.7583421577
C23	-0.9406249908	-5.1057870218	-0.8993867291
C24	-1.6506730984	5.1303073985	-1.9756315971
C25	0.7054342210	5.0899163144	-0.3573517061
C26	0.9247947171	5.2271727775	-3.2117468278
C27	-1.3653637415	1.1787205985	-7.1549293788
C28	-0.2742315032	-1.4644189960	-7.1716867589
C29	1.4730508830	0.7990394757	-7.1599437521
C30	0.2375861262	1.6471815444	2.9998639490
C31	1.3115824667	-1.0018836453	3.0293831845
C32	-1.5283278396	-0.5997056959	3.0362594810
C33	5.0745151479	-1.5333695820	-1.4693894730
C34	4.9670844011	-0.0417592572	-3.9073820583
C35	5.1414018966	1.3313062565	-1.4067525930
C36	-5.2157831535	-1.1341834169	-2.8063362720

C37	-5.1082926179	1.7206640990	-2.5731379321
C38	-5.0200644372	0.0860804877	-0.2277611661
H39	-0.6432979603	-6.0752911680	-3.7192046909
H40	-1.7989311798	-4.7149461699	-3.8548575507
H41	-0.2164588039	-4.5981086763	-4.6325554647
H42	-0.8364016302	-6.1896755345	-1.0222580515
H43	-0.5327797822	-4.8053423635	0.0685826186
H44	-1.9974930456	-4.8316863810	-0.9170653808
H45	1.5418084277	-6.0815494103	-2.2243142340
H46	2.2364720352	-4.6156904151	-2.9783791626
H47	2.1040789864	-4.7146878657	-1.2157970028
H48	-6.1939001930	1.6730651451	-2.4322846284
H49	-4.7080667118	2.5915189601	-2.0487519347
H50	-4.8771617277	1.8314118089	-3.6345912630
H51	-6.2961669484	-1.0226374852	-2.6613087660
H52	-4.9797016431	-1.0956962662	-3.8717937604
H53	-4.8927010251	-2.1062436057	-2.4263726107
H54	-6.1139545402	0.1306554694	-0.2702395630
H55	-4.7068916895	-0.8520034200	0.2354283665
H56	-4.6407926082	0.9112398694	0.3789968645
H57	-1.2936362932	1.0987853074	-8.2454708581

H58	-2.3469874821	0.8310643352	-6.8248203617
H59	-1.2616476055	2.2232674084	-6.8538636124
H60	-0.2517303324	-1.3506789391	-8.2611629620
H61	0.5257439418	-2.1377080749	-6.8555516008
H62	-1.2279257611	-1.8993017802	-6.8652684044
H63	1.3851780083	0.7295571571	-8.2499476051
H64	1.6412202492	1.8376157854	-6.8679956637
H65	2.3295084689	0.2106553551	-6.8224904981
H66	-1.4335063116	-0.5209582435	4.1250112927
H67	-2.3763204981	0.0002789392	2.6977854682
H68	-1.7155957485	-1.6379172213	2.7545673769
H69	1.2398802683	-0.9096158538	4.1189359103
H70	1.2083764040	-2.0497848382	2.7398947345
H71	2.2932295556	-0.6575748159	2.6956201775
H72	0.2118429950	1.5550428290	4.0913188290
H73	1.1962899785	2.0660724242	2.6872851456
H74	-0.5552202385	2.3216765467	2.6686988724
H75	6.0616243492	-0.0566914954	-3.8604586243
H76	4.6099296513	-0.9116422122	-4.4627651682
H77	4.6331326958	0.8581789466	-4.4284504720
H78	6.1598313696	-1.4759771369	-1.6090509769

H79	4.8410361774	-1.5867256136	-0.4039584339
H80	4.6913634641	-2.4400792047	-1.9432785064
H81	6.2225510524	1.2325669521	-1.5551790835
H82	4.7963673414	2.2746795550	-1.8365276730
H83	4.9145936668	1.3461083878	-0.3387757808
H84	-1.5582274114	6.2197299213	-1.9041244150
H85	-2.1297308177	4.8613934334	-2.9194243967
H86	-2.2725757000	4.7592558293	-1.1579412645
H87	0.6110250636	6.1810991865	-0.3891494228
H88	0.1694058866	4.7001986395	0.5111675672
H89	1.7567106890	4.8122614132	-0.2572359692
H90	0.8234200223	6.3111045047	-3.0869063745
H91	1.9802677475	4.9488765518	-3.1803509545
H92	0.5294665695	4.9315164197	-4.1863488398

principal moments of inertia:

amu*angstrom^2: 12035.66319 12327.18297 12347.96481

g*cm^2: 1.99856864E-36 2.04697664E-36 2.05042754E-36

rotational constants:

cm^(-1): 0.00140064 0.00136752 0.00136522

GHz: 0.04199013 0.04099712 0.04092812

Summary for Compound 3: $Co_6S_8(PMe_3)_6$

All dft calculations were performed using Jaguar, version 7.0, Schrodinger, LLC, New York, NY, 2007

B3LYP, LCVP**/6-31G**

Final total energy = -6823.25991 hartree

HOMO energy: -0.16405 h

LUMO energy: -0.04848 h

Orbital energies (in hartrees):

-88.79474 -88.79474 -88.79298 -88.79294 -88.79293 -88.79278

-88.79273 -88.79259 -77.08906 -77.08904 -77.08900 -77.08900

-77.08899 -77.08893 -10.17230 -10.17229 -10.17228 -10.17227

-10.17221 -10.17212 -10.17200 -10.17190 -10.17185 -10.17179

-10.17172 -10.17172 -10.17036 -10.17028 -10.17025 -10.17023

-10.17018 -10.17002 -7.86866 -7.86861 -7.86729 -7.86723

-7.86723 -7.86705 -7.86693 -7.86685 -6.56652 -6.56652

-6.56646 -6.56645 -6.56645 -6.56637 -5.82872 -5.82871

-5.82870 -5.82868 -5.82845 -5.82843 -5.82741 -5.82733

-5.82732 -5.82722 -5.82721 -5.82719 -5.82712 -5.82710

-5.82708 -5.82702 -5.82697 -5.82696 -5.82696 -5.82686

-5.82685 -5.82684 -5.82663 -5.82662 -4.72832 -4.72831

-4.72828 -4.72828 -4.72826 -4.72826 -4.72825 -4.72822

-4.72822 -4.72822 -4.72817 -4.72813 -4.72543 -4.72543

-4.72537 -4.72537 -4.72537 -4.72529 -3.70461 -3.70452

-3.70448 -3.70434 -3.70421 -3.70409 -2.39810 -2.39806

-2.39791 -2.39783 -2.39754 -2.39748 -2.39537 -2.39536

-2.39528 -2.39522 -2.39521 -2.39519 -2.39479 -2.39478

-2.39477 -2.39477 -2.39474 -2.39471 -0.76317 -0.76260

-0.76249 -0.76242 -0.76222 -0.76215 -0.68735 -0.68729

-0.68723 -0.68714 -0.68709 -0.68703 -0.68606 -0.68601

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-0.63404 -0.63372 -0.61090 -0.60958 -0.60933 -0.59876

-0.53620 -0.53614 -0.53537 -0.53528 -0.53522 -0.53450

-0.43766 -0.43756 -0.43679 -0.43592 -0.43561 -0.43547

-0.42122 -0.42080 -0.42068 -0.42066 -0.42062 -0.42045

-0.42037 -0.42035 -0.42016 -0.42012 -0.42003 -0.41978

-0.39992 -0.39985 -0.39943 -0.39920 -0.39911 -0.39901

-0.39822 -0.39807 -0.39797 -0.39785 -0.39658 -0.39655

-0.38010 -0.37996 -0.37996 -0.37986 -0.37961 -0.37958

-0.33801 -0.33795 -0.33219 -0.33201 -0.33193 -0.33190

-0.33169 -0.33157 -0.33089 -0.33088 -0.33002 -0.32947

-0.32938 -0.32933 -0.32698 -0.31477 -0.31461 -0.31451

-0.29618 -0.29381 -0.29365 -0.29080 -0.29014 -0.29000

-0.28337 -0.28286 -0.28263 -0.28200 -0.27799 -0.27784

-0.26538	-0.26495	-0.26456	-0.24915	-0.24434	-0.24404
-0.23749	-0.23735	-0.23732	-0.23666	-0.23652	-0.23628
-0.22636	-0.22622	-0.22573	-0.21830	-0.21725	-0.21704
-0.19694	-0.19547	-0.19531	-0.18815	-0.18783	-0.18677
-0.18120	-0.17956	-0.17946	-0.17542	-0.16554	-0.16528
-0.16405	-0.04848	-0.04825	-0.04802	-0.03648	-0.03644
-0.02440	-0.02434	-0.02375	-0.02210	-0.02200	

final geometry:

angstroms

atom	x	y	z
S1	-0.0072388403	-0.0011455994	-0.0030889487
Co2	0.0014981382	0.0026026736	2.2774574934
P3	2.1257549511	0.0049312337	2.7193744237
Co4	-1.6656529149	-1.4603636108	0.5461695464
P5	-1.2709587228	-2.9887726966	-0.9411949480
Co6	-1.7475267861	1.3645133804	0.5276265304
P7	-1.4926977520	2.9511579826	-0.9304756297
Co8	-2.1639086697	-1.4551454807	3.3170458992
P9	-2.4055456608	-3.0364805911	4.7821298109

Co10	-3.9134738044	-0.0943991275	1.5665289256
P11	-6.0373790109	-0.0979307033	1.1255627634
S12	-3.1131857787	-0.1001436059	-0.5670365964
S13	-3.4602329055	-2.3242874309	1.6588028348
S14	-0.3279691406	-2.2592312472	2.2186997846
Co15	-2.2449154883	1.3675837714	3.2975053145
P16	-2.6359770783	2.8966260552	4.7846576903
S17	-0.4511158332	2.2332691668	2.1854239371
S18	-3.5835127044	2.1657993307	1.6256024531
S19	-0.7973519490	0.0087615121	4.4110509675
S20	-3.9048077964	-0.0897762487	3.8462921772
C21	-6.5495464680	1.0102536499	-0.2541017757
C22	-7.1411086371	0.4413592323	2.4981565714
C23	-6.7655839931	-1.7158320241	0.6284725877
C24	2.6384162847	-1.1109875039	4.0927080655
C25	3.2314700625	-0.5247475269	1.3444639435
C26	2.8522751139	1.6203939568	3.2270954796
C27	-2.0474837077	2.5440737041	6.4946148870
C28	-4.4164409987	3.2883369815	5.0495551953
C29	-1.9105883468	4.5536618935	4.4372412523
C30	0.5111385845	-3.3655821730	-1.2170499072

C31	-1.8744011634	-2.6452636934	-2.6479251233
C32	-1.9782779355	-4.6519518262	-0.5855421381
C33	-2.6636392746	2.9378574225	-2.3528781682
C34	-1.6886893241	4.6592359761	-0.2678344046
C35	0.1524902656	3.0345774897	-1.7561562039
C36	-4.0094641692	-3.0690504710	5.6883164464
C37	-1.1661315629	-3.0644037052	6.1443979146
C38	-2.2966318578	-4.7476985294	4.1082138740
H39	-8.1909230463	0.4366147163	2.1846130169
H40	-7.0043466736	-0.2234020068	3.3536306880
H41	-6.8530218442	1.4490077539	2.8068998048
H42	-7.8323964989	-1.6135526570	0.4006200207
H43	-6.2340649924	-2.0883828127	-0.2503269261
H44	-6.6247137471	-2.4383838324	1.4350755826
H45	-7.6324294208	0.9645414897	-0.4144823264
H46	-6.2532763138	2.0334607703	-0.0115405871
H47	-6.0254878158	0.7089519664	-1.1638719039
H48	3.7215918369	-1.0672387937	4.2516421373
H49	2.1161432983	-0.8136207433	5.0047676920
H50	2.3406391782	-2.1325846020	3.8454356914
H51	3.9184785412	1.5169713793	3.4572066741

H52	2.7136155251	2.3473700843	2.4240341657
H53	2.3184183054	1.9882477305	4.1064781540
H54	4.2809649860	-0.5208175361	1.6591655793
H55	2.9448190948	-1.5308821195	1.0292983053
H56	3.0948963128	0.1450043634	0.4927333219
H57	-2.3157476623	3.3573919251	7.1780442025
H58	-2.4962388787	1.6092128765	6.8383965739
H59	-0.9637688404	2.4096991192	6.4831782160
H60	-2.1772819612	5.2728816736	5.2195967093
H61	-0.8244589979	4.4639642999	4.3672257231
H62	-2.2814413202	4.9048532489	3.4713606896
H63	-4.5387193466	4.0755371374	5.8017511841
H64	-4.8507501717	3.6113419386	4.1005439531
H65	-4.9339260687	2.3819862389	5.3716495788
H66	-1.7089370295	-5.3706554549	-1.3674599489
H67	-1.5988402908	-4.9969208815	0.3792269143
H68	-3.0648108461	-4.5726391322	-0.5098876678
H69	-1.6067003626	-3.4591584324	-3.3309018796
H70	-2.9588051615	-2.5173208171	-2.6285434809
H71	-1.4340047323	-1.7088536008	-2.9983865089
H72	0.6352015585	-4.1554444084	-1.9661628146

H73	1.0185084487	-2.4563738586	-1.5470870978
H74	0.9546293421	-3.6800108066	-0.2693802438
H75	-4.0518968666	-3.9167809591	6.3811485593
H76	-4.1343764114	-2.1330643835	6.2366850192
H77	-4.8235579841	-3.1430963436	4.9635146538
H78	-2.4214487732	-5.4926774578	4.9018626461
H79	-3.0718121888	-4.8781656962	3.3498548460
H80	-1.3236999341	-4.8759940605	3.6282355195
H81	-1.3443301825	-3.9065074073	6.8222648866
H82	-0.1667807029	-3.1451319526	5.7103387974
H83	-1.2164686478	-2.1237346782	6.6967472368
H84	0.2024416969	3.8824221837	-2.4483142095
H85	0.9258308980	3.1363683841	-0.9911040833
H86	0.3347645823	2.1023023732	-2.2946266477
H87	-1.5440308713	5.4065161620	-1.0559848217
H88	-2.6885396281	4.7598051248	0.1604051593
H89	-0.9578478216	4.8138703966	0.5292579349
H90	-2.4781464732	3.7840302128	-3.0237170620
H91	-2.5570835932	1.9986626792	-2.8999118863
H92	-3.6856872626	2.9878443762	-1.9700641084

principal moments of inertia:

amu*angstrom^2: 9301.13767 9495.13624 9517.05244

g*cm^2: 1.54449005E-36 1.57670427E-36 1.58034354E-36

rotational constants:

cm^(-1): 0.00181243 0.00177540 0.00177131

GHz: 0.05433518 0.05322504 0.05310247

VIII. **References**

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