

Supporting Information

Structural Evolution and Electronic Properties of CoSi_n^- ($n = 3-12$) Clusters: Mass-Selected Anion Photoelectron Spectroscopy and Quantum Chemistry Calculations

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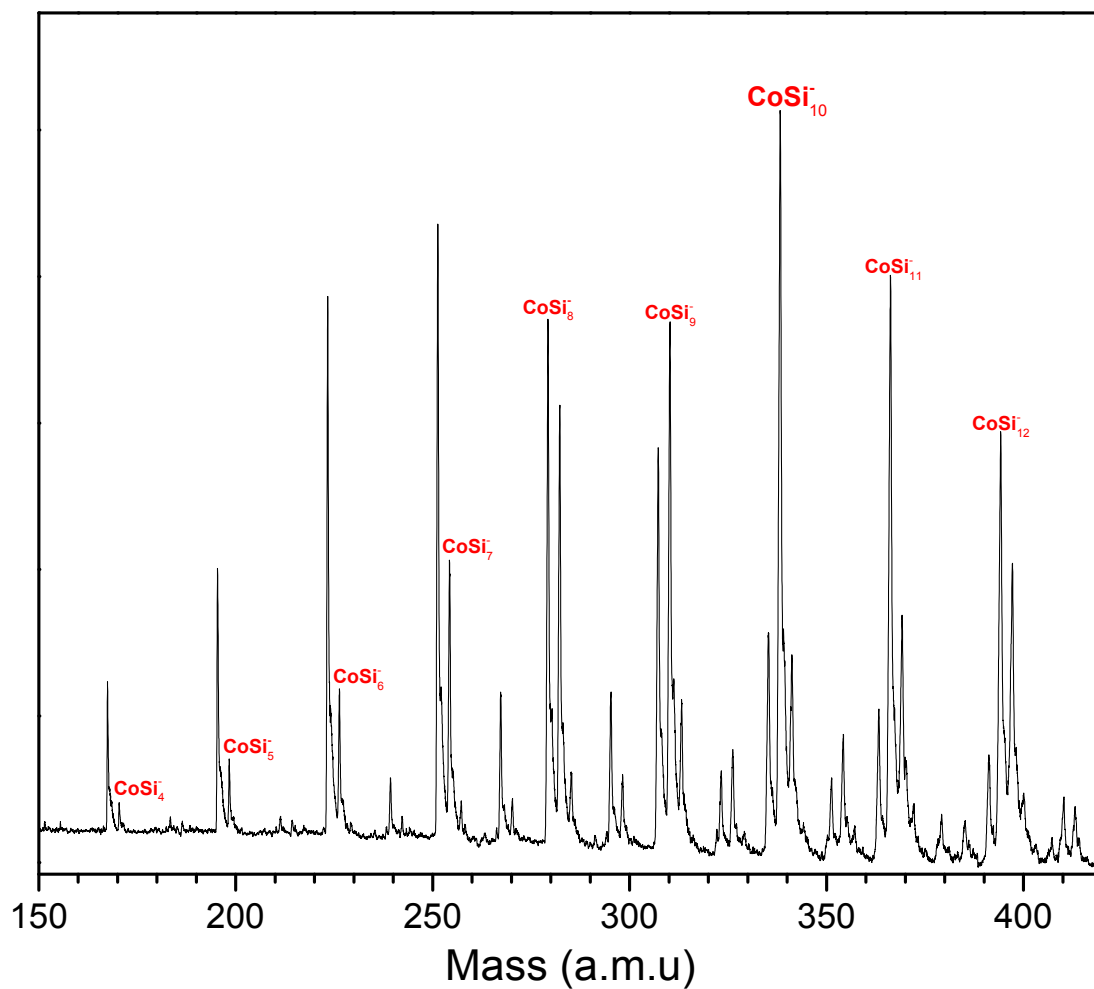


Fig. S1 Mass spectra of Co-Si clusters anions (Co_nSi_m^-) produced by laser ablation on mixed samples of cobalt powder and isotopically enriched silicon powder (Co: ^{28}Si mole ratio 1:4).

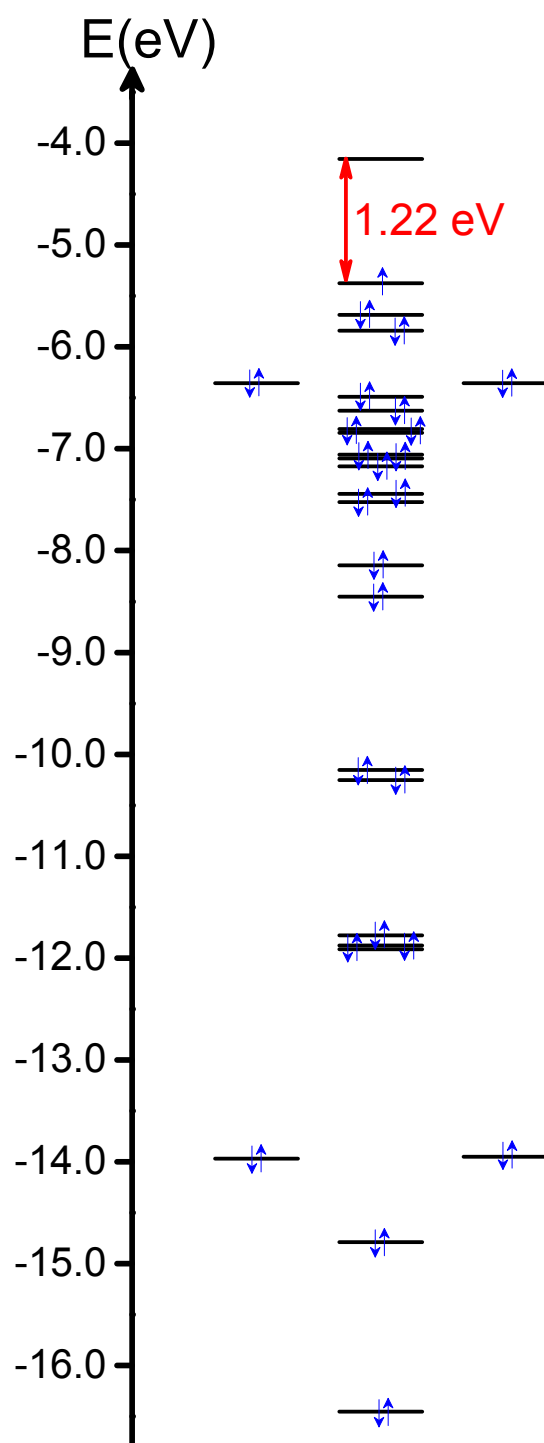


Fig. S2 Energy levels of the molecular orbitals of CoSi₁₀.

Table S1 NPA charges, and natural electron configuration of the silicon atoms of CoSi_{10}^- cluster.

Atom	NPA charge on Si atom	Natural electron configuration on Si atom
Si1	0.26	$3s^{1.56}3p^{2.14}3d^{0.01}$
Si2	0.25	$3s^{1.50}3p^{2.20}3d^{0.01}$
Si3	0.26	$3s^{1.56}3p^{2.14}3d^{0.01}$
Si4	0.28	$3s^{1.48}3p^{2.20}3d^{0.01}$
Si5	0.26	$3s^{1.56}3p^{2.14}3d^{0.01}$
Si6	0.28	$3s^{1.48}3p^{2.20}3d^{0.01}$
Si7	0.25	$3s^{1.50}3p^{2.20}3d^{0.01}$
Si8	0.28	$3s^{1.48}3p^{2.20}3d^{0.01}$
Si9	0.30	$3s^{1.48}3p^{2.19}3d^{0.01}$
Si10	0.25	$3s^{1.50}3p^{2.20}3d^{0.01}$

Table S2 Cartesian coordinates for the stable isomers of CoSi_n^- ($n = 3\text{-}12$) clusters.

CoSi_3^-							
3A				3B			
	X	Y	Z		X	Y	Z
Co	0.00000000	0.00000000	1.03484000	Co	0.40177100	0.96653800	0.00000000
Si	0.00000000	1.78187800	-0.17329400	Si	-1.57838700	-0.07267200	0.00000000
Si	0.00000000	0.00000000	-1.64917500	Si	0.40177100	-0.89568300	1.23812300
Si	0.00000000	-1.78187800	-0.17329400	Si	0.40177100	-0.89568300	-1.23812300
3C							
	X	Y	Z				
Co	-0.47647500	-0.88852000	0.00000000				
Si	0.30630500	0.10093300	1.85998800				
Si	0.30630500	1.51170800	0.00000000				
Si	0.30630500	0.10093300	-1.85998800				

CoSi₄⁻

4A				4B			
	X	Y	Z		X	Y	Z
Co	-1.18523800	0.22235300	0.00000000	Co	0.000000	0.000000	1.14548900
Si	0.19769000	-1.58592000	0.00000000	Si	0.000000	1.320722	-0.92625800
Si	0.19769000	0.21977000	1.74312100	Si	0.000000	-1.320722	-0.92625800
Si	1.69274700	0.71755600	0.00000000	Si	-1.807433	0.000000	-0.17832100
Si	0.19769000	0.21977000	-1.74312100	Si	1.807433	0.000000	-0.17832100
4C				4D			
	X	Y	Z		X	Y	Z
Co	0.04653900	-0.61184500	-0.46837900	Co	-1.03669000	-0.81493300	-0.26171900
Si	1.98087400	-0.70772100	0.50115300	Si	0.32807000	1.11742100	-0.20433200
Si	-1.97835400	-0.78712300	0.34526800	Si	2.55133200	0.49142100	-0.09944200
Si	-1.19582700	1.32740200	0.14368700	Si	-1.88960900	1.10796500	0.35139500
Si	1.10355300	1.34742700	-0.08680700	Si	1.00953800	-1.14514900	0.45712200

CoSi₅⁻

5A				5B			
	X	Y	Z		X	Y	Z
Co	0.00000000	0.00000000	0.16659800	Co	0.00000000	0.00000000	1.32309700
Si	0.00000000	1.21580000	1.91591500	Si	0.00000000	1.72422600	-0.14802900
Si	0.00000000	-1.21580000	1.91591500	Si	-1.72422600	0.00000000	-0.14802900
Si	-1.91709600	0.00000000	-0.94832100	Si	1.72422600	0.00000000	-0.14802900
Si	0.00000000	0.00000000	-2.25648300	Si	0.00000000	-1.72422600	-0.14802900
Si	1.91709600	0.00000000	-0.94832100	Si	0.00000000	0.00000000	-1.95957100
5C				5D			
	X	Y	Z		X	Y	Z
Co	0.12220400	0.85821200	0.00000000	Co	0.73117400	0.13112500	0.00000000
Si	1.91460200	1.91450200	0.00000000	Si	-1.22366400	-1.28502700	0.00000000
Si	0.12220400	-0.53511700	1.70959900	Si	0.42241500	-1.16816300	1.72663200
Si	0.12220400	-0.53511700	-1.70959900	Si	0.42241500	-1.16816300	-1.72663200
Si	-1.81913400	-0.29847500	0.00000000	Si	0.42241500	2.31828700	0.00000000
Si	-0.57555500	-2.20091500	0.00000000	Si	-1.45370300	1.05018300	0.00000000

CoSi₆⁻

6A				6B			
	X	Y	Z		X	Y	Z
Co	-0.50055300	0.23071600	0.00000000	Co	-1.01462200	0.74088900	0.00000000
Si	0.37313700	-1.33064500	1.45083300	Si	-0.08938600	2.66921700	0.00000000
Si	0.37313700	1.00044400	1.90158900	Si	1.66386100	-1.62065100	0.00000000
Si	0.37313700	-1.33064500	-1.45083300	Si	1.32905400	0.72631300	0.00000000
Si	0.37313700	1.00044400	-1.90158900	Si	-0.76798600	-2.17395000	0.00000000
Si	0.80170500	2.29335900	0.00000000	Si	-0.08938600	-0.51489300	1.58789600
Si	-1.32890200	-2.07790900	0.00000000	Si	-0.08938600	-0.51489300	-1.58789600
6C				6D			
	X	Y	Z		X	Y	Z
Co	0.00000000	0.00000000	1.16489900	Co	0.00000000	0.00000000	0.00000000
Si	0.00000000	2.00447100	-0.08780000	Si	0.00000000	0.00000000	2.48953300
Si	-1.17819800	-1.62165100	-0.08780000	Si	0.00000000	0.00000000	-2.48953300
Si	1.90636500	0.61941500	-0.08780000	Si	0.00000000	1.87866700	1.16421800
Si	1.17819800	-1.62165100	-0.08780000	Si	-1.87866700	0.00000000	-1.16421800
Si	-1.90636500	0.61941500	-0.08780000	Si	1.87866700	0.00000000	-1.16421800
Si	0.00000000	0.00000000	-1.80759100	Si	0.00000000	-1.87866700	1.16421800

CoSi₇⁻

7A				7B			
	X	Y	Z		X	Y	Z
Co	0.41302500	-0.31973800	-0.23002300	Co	0.00000000	0.00000000	0.33433100
Si	2.33350800	1.03141400	0.38899000	Si	1.41437200	0.00000000	-1.54530800
Si	-1.36340000	1.12417100	-1.37475200	Si	0.00000000	1.89168200	-1.26363500
Si	-0.55078900	-1.59161400	1.28486100	Si	0.00000000	1.99401200	1.18592000
Si	-1.95299500	0.48474100	1.02513000	Si	0.00000000	0.00000000	2.60126300
Si	2.39118900	-1.07456400	-0.58929000	Si	0.00000000	-1.89168200	-1.26363500
Si	-1.72786300	-1.09492500	-0.85562000	Si	-1.41437200	0.00000000	-1.54530800
Si	0.07380200	1.73741400	0.56429700	Si	0.00000000	-1.99401200	1.18592000
7C				7D			
	X	Y	Z		X	Y	Z
Co	-0.14696600	0.94227500	0.00000000	Co	-0.87023100	0.31850600	0.00000000
Si	1.90094200	-0.20785900	0.00000000	Si	0.21505000	0.92543800	1.94686000
Si	-2.15655900	-0.80172100	0.00000000	Si	0.21505000	-1.41083600	1.34762900
Si	-0.14696600	-0.99829400	1.31692800	Si	0.76065000	2.24062100	0.00000000
Si	1.72150500	2.09041600	0.00000000	Si	0.21505000	-1.41083600	-1.34762900
Si	-0.14696600	-0.99829400	-1.31692800	Si	0.21505000	0.92543800	-1.94686000
Si	1.27813900	-2.48162100	0.00000000	Si	-1.70899200	-1.85859500	0.00000000
Si	-2.16665900	1.58012800	0.00000000	Si	1.76644600	-0.02549000	0.00000000

CoSi₈⁻

8A				8B			
	X	Y	Z		X	Y	Z
Co	0.53959300	-0.32130600	0.00000000	Co	0.00000000	0.00000000	1.13380900
Si	2.63200100	-0.24132500	0.00000000	Si	0.00000000	1.27140700	-0.85994000
Si	-0.49148400	1.40866700	1.32541500	Si	1.90193800	-1.22473100	0.65049900
Si	-0.49148400	-0.92113200	-1.99559600	Si	-2.11199400	0.00000000	-1.53437500
Si	-2.11448300	0.09947800	0.00000000	Si	0.00000000	-1.27140700	-0.85994000
Si	-0.49148400	-0.92113200	1.99559600	Si	-1.90193800	1.22473100	0.65049900
Si	1.43790700	1.92523400	0.00000000	Si	-1.90193800	-1.22473100	0.65049900
Si	-1.03013300	-2.13879600	0.00000000	Si	2.11199400	0.00000000	-1.53437500
Si	-0.49148400	1.40866700	-1.32541500	Si	1.90193800	1.22473100	0.65049900
8C				8D			
	X	Y	Z		X	Y	Z
Co	0.00000000	0.00000000	0.34900500	Co	-0.20299700	0.46609200	0.00000000
Si	-1.32006400	1.94337500	0.03237800	Si	0.90510300	2.02318600	1.19794300
Si	1.32006400	-1.94337500	0.03237800	Si	0.90510300	-0.24144100	-1.98573200
Si	1.32006400	1.94337500	0.03237800	Si	-2.41759100	0.01183500	0.00000000
Si	0.00000000	-1.18179300	-1.79202600	Si	-0.99543200	-1.46112100	1.34868100
Si	0.00000000	1.18179300	-1.79202600	Si	-0.99543200	-1.46112100	-1.34868100
Si	1.96193300	0.00000000	1.39072900	Si	0.90510300	2.02318600	-1.19794300
Si	-1.32006400	-1.94337500	0.03237800	Si	1.17953800	-1.55197500	0.00000000
Si	-1.96193300	0.00000000	1.39072900	Si	0.90510300	-0.24144100	1.98573200

CoSi₉⁻

9A				9B			
	X	Y	Z		X	Y	Z
Co	0.00000000	0.00000000	0.20737500	Si	-0.71455000	2.35956000	-0.57731100
Si	0.00000000	2.13621800	1.14987100	Si	1.70738700	1.75762900	-0.65773700
Si	-1.82911800	1.29965300	-0.33346200	Si	-1.82741500	0.97441000	1.07411400
Si	1.82911800	-1.29965300	-0.33346200	Si	-0.10717300	-0.41983800	2.11385800
Si	0.00000000	-1.24467100	-1.87463900	Si	1.61949200	-1.63833200	-0.53282900
Si	0.00000000	0.00000000	2.38344400	Si	-0.53823300	-2.09032700	0.42536100
Si	0.00000000	1.24467100	-1.87463900	Si	-2.16746700	-0.71587300	-0.66551200
Si	0.00000000	-2.13621800	1.14987100	Si	-0.14924800	-0.91501800	-2.02760000
Si	-1.82911800	-1.29965300	-0.33346200	Si	2.05332100	0.10886100	1.10211900
Si	1.82911800	1.29965300	-0.33346200	Co	0.06423700	0.30018500	-0.13194400
9C				9D			
	X	Y	Z		X	Y	Z
Co	-0.05831900	0.20803700	-0.07805800	Co	-0.21798600	0.15294400	0.00000000
Si	1.99306100	-0.18414900	-1.27741200	Si	1.58991300	-1.67452900	0.00000000
Si	-2.22776900	-0.86031000	0.78600800	Si	-1.24222300	2.10183500	0.00000000
Si	1.64543900	-1.15469700	1.14674400	Si	1.04541000	-0.37863300	1.89944200
Si	-2.04517300	1.32453500	-0.14227100	Si	1.04541000	-0.37863300	-1.89944200
Si	-0.37040600	-0.24683500	2.14430800	Si	-0.82198200	-1.71609600	-1.29879900
Si	0.07963000	2.39245200	-0.64494400	Si	-2.46496600	-0.27333200	0.00000000
Si	-1.50332700	-0.94872000	-1.53754000	Si	-0.82198200	-1.71609600	1.29879900
Si	0.57163600	-2.00278700	-0.91814000	Si	1.04541000	1.87026100	1.17811800
Si	1.96938100	1.27929500	0.59378900	Si	1.04541000	1.87026100	-1.17811800

CoSi₁₀⁻

10A				10B			
	X	Y	Z		X	Y	Z
Si	1.29178000	0.74580900	-1.75987700	Co	0.00000000	0.00000000	0.08372300
Si	0.00000000	2.31126600	-0.10678800	Si	-1.84489100	1.06514800	-1.19431600
Si	0.00000000	-1.49161900	-1.75987700	Si	1.84489100	1.06514800	-1.19431600
Si	-1.79813400	1.03815300	1.05042000	Si	0.00000000	2.29351500	-0.14942900
Si	-1.29178000	0.74580900	-1.75987700	Si	0.00000000	0.00000000	-2.29256100
Si	1.79813400	1.03815300	1.05042000	Si	-1.19480300	-0.68982000	2.05411000
Si	2.00161500	-1.15563300	-0.10678800	Si	1.98624200	-1.14675700	-0.14942900
Co	0.00000000	0.00000000	0.04477400	Si	1.19480300	-0.68982000	2.05411000
Si	0.00000000	-2.07630600	1.05042000	Si	0.00000000	-2.13029700	-1.19431600
Si	0.00000000	0.00000000	2.36238300	Si	-1.98624200	-1.14675700	-0.14942900
Si	-2.00161500	-1.15563300	-0.10678800	Si	0.00000000	1.37964000	2.05411000
10C				10D			
	X	Y	Z		X	Y	Z
Co	0.01771300	-0.00013100	0.00000000	Co	0.00000000	0.00000000	0.59369700
Si	-0.68216700	1.92625600	1.21850900	Si	0.00000000	-1.55037800	-1.15591500
Si	-2.01453800	-0.01300000	1.21600400	Si	1.34266600	0.77518900	-1.15591500
Si	-0.68216700	1.92625600	-1.21850900	Si	-1.34266600	0.77518900	-1.15591500
Si	-2.01453800	-0.01300000	-1.21600400	Si	0.00000000	0.00000000	-3.02080400
Si	1.65990600	1.26947200	1.21513700	Si	1.74325800	1.00647000	1.47490200
Si	1.67714700	-1.24720600	-1.21500900	Si	-1.74325800	1.00647000	1.47490200
Si	1.67714700	-1.24720600	1.21500900	Si	0.00000000	-2.01294100	1.47490200
Si	1.65990600	1.26947200	-1.21513700	Si	0.00000000	2.42516000	0.30628500
Si	-0.65742900	-1.93539600	-1.21888800	Si	-2.10025000	-1.21258000	0.30628500
Si	-0.65742900	-1.93539600	1.21888800	Si	2.10025000	-1.21258000	0.30628500

CoSi₁₁⁻

11A				11B			
	X	Y	Z		X	Y	Z
Co	0.00000000	0.00000000	0.07163800	Co	0.00000000	0.00000000	0.10597800
Si	-2.05827400	0.00000000	-0.95357000	Si	-1.91915300	0.62357100	1.46989400
Si	2.05827400	0.00000000	-0.95357000	Si	0.00000000	2.01791700	1.46989400
Si	0.00000000	2.09454600	-1.39438000	Si	1.91915300	0.62357100	1.46989400
Si	1.36715800	-1.94398800	0.58310500	Si	1.18610200	-1.63252900	1.46989400
Si	0.00000000	0.00000000	-2.54308900	Si	-1.18610200	-1.63252900	1.46989400
Si	-1.36715800	-1.94398800	0.58310500	Si	0.00000000	2.17217000	-1.04296500
Si	1.36715800	1.94398800	0.58310500	Si	2.06585700	0.67123800	-1.04296500
Si	-1.36715800	1.94398800	0.58310500	Si	1.27677000	-1.75732300	-1.04296500
Si	0.00000000	-2.09454600	-1.39438000	Si	-1.27677000	-1.75732300	-1.04296500
Si	0.00000000	1.19828900	2.38420300	Si	-2.06585700	0.67123800	-1.04296500
Si	0.00000000	-1.19828900	2.38420300	Si	0.00000000	0.00000000	-2.33903300
11C				11D			
	X	Y	Z		X	Y	Z
Co	0.00000000	0.00000000	0.00322700	Co	-0.00499800	0.29187600	0.00000000
Si	0.00000000	1.23979600	-2.13932000	Si	1.31898900	-0.16365700	2.03664300
Si	-2.00364600	1.21928800	-0.82956800	Si	-0.30856000	-1.74000600	1.26932800
Si	2.00364600	1.21928800	-0.82956800	Si	-0.30856000	-1.74000600	-1.26932800
Si	1.16949300	1.82437900	1.29773500	Si	1.31898900	-0.16365700	-2.03664300
Si	-1.16949300	-1.82437900	1.29773500	Si	2.29012500	0.80690200	0.00000000
Si	-2.00364600	-1.21928800	-0.82956800	Si	-1.98171100	0.06699500	-1.22068200
Si	2.00364600	-1.21928800	-0.82956800	Si	-0.30856000	1.64676400	-1.91251700
Si	-1.16949300	1.82437900	1.29773500	Si	0.71673500	2.70470800	0.00000000
Si	1.16949300	-1.82437900	1.29773500	Si	-0.30856000	1.64676400	1.91251700
Si	0.00000000	0.00000000	2.39974700	Si	-1.98171100	0.06699500	1.22068200
Si	0.00000000	-1.23979600	-2.13932000	Si	-0.43754000	-3.69470700	0.00000000

CoSi₁₂⁻

12A				12B			
	X	Y	Z		X	Y	Z
Co	0.00000000	0.00000000	0.00000000	Co	0.17231000	0.28292300	0.00000000
Si	-1.22073200	1.96085400	1.06075300	Si	-1.25526200	1.04741500	1.99121000
Si	0.00000000	-1.16626200	-2.39019300	Si	1.16946600	1.26387800	-1.95381200
Si	-1.96085400	-1.22073200	-1.06075300	Si	1.16946600	1.26387800	1.95381200
Si	0.00000000	1.16626200	-2.39019300	Si	-1.10499600	-1.25310500	-1.38341300
Si	1.22073200	1.96085400	1.06075300	Si	-1.20303000	2.33975200	0.00000000
Si	1.22073200	-1.96085400	1.06075300	Si	0.98900800	-2.18132000	0.00000000
Si	-1.16626200	0.00000000	2.39019300	Si	-1.23680300	-3.24157200	0.00000000
Si	1.96085400	-1.22073200	-1.06075300	Si	1.16946600	-1.10873600	2.09766200
Si	-1.96085400	1.22073200	-1.06075300	Si	-1.10499600	-1.25310500	1.38341300
Si	1.16626200	0.00000000	2.39019300	Si	1.16946600	-1.10873600	-2.09766200
Si	1.96085400	1.22073200	-1.06075300	Si	1.16116400	2.63859900	0.00000000
Si	-1.22073200	-1.96085400	1.06075300	Si	-1.25526200	1.04741500	-1.99121000
12C				12D			
	X	Y	Z		X	Y	Z
Co	0.00957600	0.26052200	0.00000000	Si	-1.86431100	1.40689700	1.16661100
Si	1.70690100	-0.12673300	1.87923900	Si	1.87674900	1.08457200	-1.54059800
Si	-1.55414600	-0.17722700	-1.95734700	Si	0.31860300	2.14323000	1.54190200
Si	0.24337900	-3.76556000	0.00000000	Si	1.99224500	-1.21672400	-1.16874200
Si	-1.55414600	-0.17722700	1.95734700	Si	-0.31860300	-2.14323000	1.54190200
Si	-0.79143700	2.58537500	0.00000000	Co	0.00000000	0.00000000	-0.00012200
Si	0.05806100	1.60103100	-2.06265800	Si	0.00000000	2.40990800	-0.83781000
Si	0.05806100	1.60103100	2.06265800	Si	-1.99224500	1.21672400	-1.16874200
Si	0.05806100	-1.81394100	1.24788400	Si	0.00000000	-2.40990800	-0.83781000
Si	0.05806100	-1.81394100	-1.24788400	Si	2.24106100	0.88541800	0.83875500
Si	1.70690100	-0.12673300	-1.87923900	Si	-2.24106100	-0.88541800	0.83875500
Si	2.42835700	0.97730600	0.00000000	Si	1.86431100	-1.40689700	1.16661100
Si	-2.43652100	0.73418600	0.00000000	Si	-1.87674900	-1.08457200	-1.54059800