Supporting Information

Structural and Electronic Properties of Ruthenium Doped Germanium Clusters

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Table S1. Electronic states (State), point group symmetries (Sym.), relative energies (ΔE, kcal/mol), HOMO–LUMO gaps (E_{gap}, eV), and charges on Ru atom (Q, e) of the low-lying $RuGe_n^{2-}$ and $RuGe_n^{3-}$ (n = 2-12) isomers.

$RuGe_n^{2-}$						$RuGe_n^{3-}$					
Iso.	State	Sym.	ΔE	E_{gap}	Q	Iso.	State	Sym.	ΔE	E_{gap}	Q
2d.1	**$^3B_1$**	***C_{2v}***	**0.00**	**0.65**	**-1.48**	**2t.1**	**$^4A_2$**	***C_{2v}***	**0.00**	**0.54**	**-2.25**
2d.2	$^3A_2$	C_{2v}	6.33			2t.2	$^2A_1$	C_{2v}	4.02		
2d.3	$^3\Sigma_g$	$D_{\infty v}$	33.77			2t.3	$^4\Sigma_g$	$C_{\infty v}$	13.55		
3d.1	**$^3B_1$**	***C_{2v}***	**0.00**	**0.66**	**-1.30**	**3t.1**	**$^2A_1$**	***C_{2v}***	**0.00**	**0.53**	**-1.91**
3d.2	^3A	C_s	9.56			3t.2	$^4A''$	C_s	4.26		
3d.3	$^3A'$	C_s	30.82			3t.3	$^4A''$	C_s	13.95		
4d.1	**$^3A''$**	***C_s***	**0.00**	**0.33**	**-1.70**	**4t.1**	**^2A**	***C_s***	**0.00**	**0.43**	**-1.87**
4d.2	$^3B_2$	C_{2v}	7.82			4t.2	$^2A''$	C_s	14.74		
4d.3	$^3A'$	C_s	16.67			4t.3	$^4A''$	C_s	34.92		
5d.1	**^1A**	***C_1***	**0.00**	**0.47**	**-1.38**	**5t.1**	**$^2A'$**	***C_s***	**0.00**	**0.65**	**-1.68**
5d.2	^3A	C_1	2.19			5t.2	$^2A'$	C_s	18.34		
5d.3	$^1A'$	C_s	53.46			5t.3	$^4A'$	C_s	27.47		
6d.1	**$^1A_1$**	***C_{5v}***	**0.00**	**0.78**	**-1.44**	**6t.1**	**$^2A'$**	***C_s***	**0.00**	**0.33**	**-1.71**
6d.2	$^3A''$	C_s	21.97			6t.2	$^4A_1$	C_{5v}	6.63		
6d.3	$^1A'$	C_s	25.89			6t.3	$^4A_1$	C_{3v}	9.35		
7d.1	**^1A**	***C_2***	**0.00**	**0.89**	**-2.15**	**7t.1**	**$^2A'$**	***C_s***	**0.00**	**0.25**	**-2.04**
7d.2	$^1A'$	C_s	5.79			7t.2	$^2A''$	C_s	3.99		
7d.3	$^1A'$	C_s	10.47			7t.3	$^2A''$	C_s	19.42		
8d.1	**$^1A'$**	***C_s***	**0.00**	**1.12**	**-2.27**	**8t.1**	**^2A**	***C_s***	**0.00**	**0.38**	**-2.15**
8d.2	^1A	C_1	5.63			8t.2	$^2A''$	C_1	5.72		
8d.3	^3A	C_{3v}	26.45			8t.3	$^2A'$	C_s	5.86		
9d.1	**$^1A'$**	***C_s***	**0.00**	**1.33**	**-2.61**	**9t.1**	**$^2A'$**	***C_s***	**0.00**	**0.39**	**-2.41**
9d.2	$^3A_1$	C_{3v}	18.64			9t.2	$^2A'$	C_s	4.81		
9d.3	$^3A'$	C_{3h}	21.65			9t.3	$^4A_1$	C_{3v}	14.53		
10d.1	**$^1A_1$**	***C_{3v}***	**0.00**	**1.15**	**-2.79**	**10t.1**	**^2A**	***C_1***	**0.00**	**0.17**	**-2.62**
10d.2	$^3B_2$	C_{2v}	13.77			10t.2	$^2A_1'$	D_{5h}	0.97		
10d.3	$^1A'$	C_s	18.64			10t.3	^2A	C_1	21.58		
11d.1	**$^1A'$**	***C_s***	**0.00**	**1.33**	**-2.78**	**11t.1**	**$^2A_2$**	***C_{2v}***	**0.00**	**0.29**	**-2.72**
11d.2	$^1A'$	C_s	21.63			11t.2	$^4A''$	C_s	27.08		
11d.3	$^1A'$	C_s	44.93			11t.3	^2A	C_1	38.78		
12d.1	**^1A**	***S_4***	**0.00**	**0.98**	**-2.42**	**12t.1**	**$^2A_2$**	***D_{2d}***	**0.00**	**0.21**	**-2.22**
12d.2	$^1A'$	C_s	9.68			12t.2	$^2A_1'$	D_{5h}	12.54		
12d.3	$^1A'$	C_s	19.84			12t.3	^2A	C_1	24.64		

Table S2. The calculated bond lengths (Å) and bond angles (°) of the ground state $RuGe_{12}^{3-}$ cluster in Figure S1, together with the available experimental and theoretical data for comparison.

Bond length (Å)				Bond angle (°)			
	This work	Theo.[1]	Exp.[1]		This work		This work
Ge-Ge				Ge-Ge-Ge		Ge-Ru-Ge	
1-2	2.493	2.562	2.442	4-5-7	103.295	4-13-5	54.623
1-3	2.535	2.606	2.489	5-7-9	113.588	5-13-7	54.474
1-11	2.535	2.606	2.489	7-9-3	103.295	7-13-9	54.474
2-4	2.535	2.606	2.479	9-3-4	108.619	9-13-3	54.623
2-12	2.535	2.606	2.474	3-4-5	108.619	3-13-4	57.605
3-4	2.638	2.719	2.577	5-6-8	88.362	5-13-6	57.605
3-9	2.512	2.575	2.466	6-8-7	91.638	6-13-8	54.474
4-5	2.512	2.575	2.466	8-7-5	91.638	8-13-7	52.871
5-6	2.638	2.719	2.601	7-5-6	88.362	8-13-10	54.474
5-7	2.535	2.606	2.485	7-8-10	91.638	9-13-10	57.605
6-8	2.535	2.606	2.478	8-10-9	88.362	10-13-11	54.623
6-12	2.512	2.575	2.467	10-9-7	88.362	11-13-1	54.474
7-8	2.493	2.562	2.451	9-7-8	91.638	1-13-3	54.474
7-9	2.535	2.606	2.485	3-9-10	108.619	4-13-2	54.474
8-10	2.535	2.606	2.487	9-10-11	108.619	2-13-1	52.871
9-10	2.638	2.719	2.599	10-11-1	103.295	2-13-12	54.474
10-11	2.512	2.575	2.478	11-1-3	113.588	12-13-6	54.623
11-12	2.638	2.719	2.585	1-3-9	103.295	11-13-12	57.605
				1-3-4	88.362		
Ru-Ge				3-4-2	88.362		
13-1	2.800	2.887	2.771	4-2-1	91.638		
13-2	2.800	2.887	2.735	2-1-3	91.638		
13-3	2.737	2.811	2.713	2-4-5	103.295		
13-4	2.737	2.811	2.675	4-5-6	108.619		
13-5	2.737	2.811	2.684	5-6-12	108.619		
13-6	2.737	2.811	2.667	6-12-2	103.295		
13-7	2.800	2.887	2.725	12-2-4	113.588		
13-8	2.800	2.887	2.721	1-2-12	91.638		
13-9	2.737	2.811	2.708	2-12-11	88.362		
13-10	2.737	2.811	2.705	12-11-1	88.362		
13-11	2.737	2.811	2.714	11-1-2	91.638		
13-12	2.737	2.811	2.651	6-8-10	113.588		
				8-10-11	103.295		
				10-11-12	108.619		
				11-12-6	108.619		
				12-6-8	103.295		

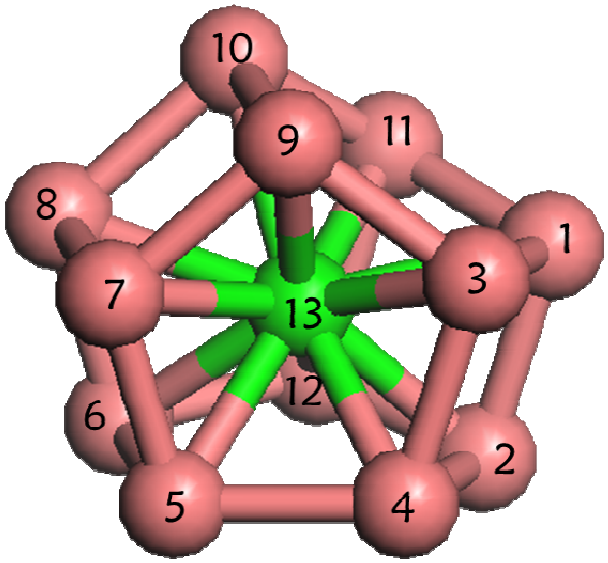

Figure S1. The structure of ground state $RuGe_{12}^{3-}$ (D_{2d}) cluster. The green balls labeled 1-12 are Ge atoms and the red ball labled 13 is Ru atom.

Reference

[1] Espinoza-Quintero, G.; Duckworth, J. C. A.; Myers, W. K.; McGrady, J. E.; Goicoechea, J. M. Synthesis and Characterization of $[Ru@Ge_{12}]^{3-}$: An Endohedral 3-Connected Cluster. *J. Am. Chem. Soc.* **2014**, *136*, 1210−1213.