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$Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$: A Germanium-Iron Cluster Containing Ge, Ge_2 and Ge_4 Units

Silke Wolf[a], **Wim Klopper**[b], **Claus Feldmann**[a,*]

[a] *Institut für Anorganische Chemie, Karlsruhe Institute of Technology (KIT), Engesserstrasse 15, D-76131 Karlsruhe, Germany*
**claus.feldmann@kit.edu*

[b] *Institut für Physikalische Chemie, Karlsruher Institut für Technologie (KIT), Fritz-Haber-Weg 2, D-76131 Karlsruhe, Germany*

Supplementary Information

Content

1. Materials and Synthesis

Motivation: In our previous work, we studied intensely the reactivity of $Fe(CO)_5$ with SnI_4 in ILs[1a,b] leading, for instance, to the adamantan-like $[\{Fe(CO)_3\}_4\{SnI\}_6I_4]^{2-}$ cluster.[1a] The course of reaction including a redox reaction between the zero-valent metal carbonyl and a main-group halide turned out as highly promising in view of the synthesis and crystallization of novel metal carbonyl clusters. This strategy was explored for several systems, for instance, $PbI_2/Mn_2(CO)_{10}$ resulting in a $[(Pb_6I_6)\{Mn(CO)_5\}_6]^{2-}$ cluster[1c] or $GeI_4/Fe_2(CO)_9$ leading to the already presented molecular compounds $FeI_4\{GeI_3Fe(CO)_3\}_2$ and $(GeI_3)_2Fe(CO)_4$.[1d]

General considerations: All reactions and sample handling were carried out under dried argon atmosphere using standard Schlenk techniques or glove-boxes. Reactions were performed in Schlenk flasks and glass ampoules that were evacuated ($p < 10^{-3}$ mbar), heated, and flashed with argon three times prior to use. The starting materials GeI_4 (99.999%, ABCR), $Fe_2(CO)_9$ (99%, ABCR), and $AlCl_3$ (99.99%, Sigma-Aldrich) were used as received. [BMIm]Cl (99%, Iolitec) was dried under reduced pressure (10^{-3}mbar) at 150 °C for 48 h. All compounds were handled and stored in argon-filled glove-boxes (MBraun Unilab, $c(O_2, H_2O) < 0.1$ ppm). The separation of the title compound from the ionic liquid was hampered by the fact that the ionic liquid was only soluble in polar solvents where the title compound, however, shows rapid decomposition. Therefore, crystals were separated manually from the ionic liquid for further characterization.

Synthesis of $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$: 80 mg (0.138 mmol) of GeI_4, 50.2 mg (0.138 mmol) of $Fe_2(CO)_9$, 300 mg (1.718 mmol) of [BMIm]Cl, and 572.5 mg (4.270 mmol) of $AlCl_3$ were heated under argon in a sealed glass ampoule for 96 h at 130 °C. After cooling to room temperature with a rate of 1 K/h, the title compound was obtained as dark-red crystals together with orange powder of excess GeI_4. The title compound was obtained with a yield of about 20%. The separation of the title compound from the IL and GeI_4 was hampered by the fact that the IL is only soluble in polar solvents where the title compound is as well easily dissolved and where it starts decomposing. To remove GeI_4 as a byproduct, the dark-red crystals were washed several times with a mixture of [BMIm]Cl and $AlCl_3$ as applied in the reaction. With this washing procedure far the most of the GeI_4 and parts of the title compound were dissolved. For the characterization via infrared spectroscopy, single-crystal structure analysis or energy-dispersive X-ray spectroscopy, crystals were separated manually from the IL and remaining GeI_4. The title compound is highly sensitive to oxygen and moisture.

Moreover, the compound decomposes in absence of certain CO pressure. It remains unaffected in the sealed ampoule and starts to decompose due to CO release after unsealing the ampoule under argon.

2. Analytical Equipment and Characterization

*Energy dispersive X-ray (EDXS) spectroscopy:*EDXSwas performed using an Ametec EDAX system mounted on a Zeiss SEM Supra 35 VP scanning electron microscope. Samples were prepared in the glove-box by selecting single crystals of $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$that were fixed on a conductive carbon pad on an aluminum sample holder. The samples were handled under inert conditions during transport and sample preparation.

*Single-crystal X-ray structure analysis:*For single crystal structure analysis, suitable crystals of $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$were selected, covered by inert-oil (perfluoropolyalkylether, ABCR), and placed in a glass capillary (Hilgenberg) that was sealed immediately. Data collection was performed at 200 K on an IPDS II image-plate diffractometer (Stoe, Darmstadt) using Mo-K_α radiation (λ = 71.073 pm, graphite monochromator). Data reduction and numerical absorption correction were conducted by the X-AREA software package (version 1.26).[2] Space group determination based on systematic absences of reflections, structure solution by direct methods, and refinement were performed by XPREP and SHELXTL (version 6.14, SHELXS-97).[3,4] All non-hydrogen atoms were refined anisotropically. Detailed information on crystal data and structure refinement are listed in Table S1. DIAMOND was used to prepare all illustrations.[5] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-No. 433572.

It is to be noted that X-ray powder diffraction data could not be obtained due to the low stability of the title compound (especially due to the release of CO).

Figure S1 shows the unit cell of $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$.

Table S1. Crystallographic data and refinement details of $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$.

Data	**$Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$**
Sum formula	$C_{24}O_{24}Ge_{12}I_4Fe_8$
Molar weight	2497.72 g/mol
Crystal system	Monoclinic
Space group	$P2_1/n$
Lattice parameters	a = 1184.8(1) pm b = 1854.8(1) pm c = 1219.0(1) pm α = 90° β = 110.48(1)° γ = 90°
Cell volume	$V = 2509.6\times10^6$ pm^3
Formula units per cell	Z = 2
Calculated density	$\rho = 3.305$gcm^{-3}
Measurement limits	$-16 \le h \le 16$, $-25 \le k \le 25$, $-16 \le l \le 16$
Theta range for data collection	2.29 to 59.53°
Measurement conditions	Image Plate diffractometer IPDS II (Stoe) λ(Mo-Kα) = 71.073 pm (T = 200 K)
Linear absorption coefficient	$\mu = 11.83$ mm^{-1}
Number of reflections	24341 (6774 independent)
Refinement method	Full-matrix least-squares on F^2
Merging	$R_{int} = 0.119$
Number of parameters	325
Residual electron density	1.09 to 1.04e$^-$ 10^{-6} pm^{-3}
Figures of merit	R_1 ($I \ge 4\sigma_I$) = 0.0473 R_1 = 0.0943 wR_2 (all data) = 0.094 GooF = 1.058

Table S2. Atomic coordinates (in Å) and anisotropic displacement parameters of $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$.

ATOM	x	y	z	sof	U11	U22	U33	U23	U13	U12	Ueq
I1	0.91887	0.41969	0.57123	1.00000	0.02328	0.03054	0.03231	0.00128	0.00771	0.00733	0.02925
I2	0.54662	0.69920	0.21881	1.00000	0.03055	0.02451	0.03282	0.00759	0.01437	-0.00008	0.02842
Ge1	0.65462	0.52924	0.61846	1.00000	0.01889	0.02098	0.02281	0.00240	0.00869	0.00009	0.02052
Ge2	0.56478	0.42943	0.41705	1.00000	0.02082	0.02040	0.02438	0.00407	0.01082	0.00309	0.02109
Ge3	0.49179	0.55996	0.26967	1.00000	0.01917	0.02210	0.02209	0.00030	0.00793	0.00127	0.02093
Ge4	0.56557	0.64343	0.44334	1.00000	0.01891	0.01937	0.02616	0.00003	0.00812	0.00029	0.02142
Ge5	0.75716	0.51793	0.45296	1.00000	0.02263	0.02286	0.02420	-0.00082	0.00866	0.00172	0.02311
Ge6	0.30590	0.61788	0.35689	1.00000	0.02787	0.02387	0.02763	-0.00242	0.00613	0.00481	0.02741
Fe1	0.77041	0.62340	0.56291	1.00000	0.01773	0.02020	0.02563	-0.00051	0.00792	-0.00227	0.02110
C1	0.82518	0.67815	0.47078	1.00000	0.03395	0.03026	0.03679	-0.00844	0.01834	-0.00634	0.03208
O1	0.86153	0.71381	0.41412	1.00000	0.03864	0.04727	0.05147	0.01437	0.02441	-0.00342	0.04349
C2	0.91455	0.59688	0.66584	1.00000	0.03239	0.01658	0.04096	-0.00597	0.01529	-0.00325	0.02933
O2	1.00585	0.58285	0.73316	1.00000	0.02295	0.05674	0.05151	-0.00035	0.00180	0.00159	0.04672
C3	0.75003	0.69346	0.65221	1.00000	0.01983	0.03333	0.03265	-0.00957	0.00749	-0.00929	0.02906
O3	0.73854	0.74234	0.70571	1.00000	0.05237	0.03982	0.04860	-0.02468	0.01881	-0.01202	0.04663
Fe2	0.27481	0.54183	0.19988	1.00000	0.01787	0.02442	0.02046	0.00087	0.00556	0.00062	0.02122
C4	0.27190	0.45488	0.13638	1.00000	0.01865	0.04829	0.03296	-0.00024	0.00995	0.00129	0.03306
O4	0.26523	0.39823	0.09927	1.00000	0.05143	0.03855	0.06660	-0.02288	0.02768	-0.00771	0.05032
C5	0.11363	0.54369	0.15785	1.00000	0.02472	0.05014	0.02557	0.00163	0.01182	0.00301	0.03268
O5	0.01142	0.54523	0.12027	1.00000	0.01482	0.10703	0.04126	0.00276	0.00520	0.00972	0.05559
C6	0.27083	0.59980	0.08050	1.00000	0.02706	0.04129	0.02093	-0.00079	0.00407	-0.00043	0.03091
O6	0.26429	0.63322	0.00191	1.00000	0.04423	0.07467	0.03830	0.02755	0.00463	-0.00483	0.05501
Fe3	0.64127	0.47413	0.26722	1.00000	0.01963	0.02236	0.01971	0.00023	0.00872	0.00212	0.02008
C7	0.27048	0.73040	0.51123	1.00000	0.03235	0.01787	0.03361	0.00016	0.01570	0.00156	0.02683
O7	0.18549	0.75815	0.51182	1.00000	0.04189	0.03843	0.05182	-0.00563	0.02459	0.01156	0.04187
C8	0.48366	0.71387	0.65816	1.00000	0.03501	0.02748	0.03158	-0.00758	0.01105	-0.00586	0.03152
O8	0.52283	0.72749	0.75547	1.00000	0.04841	0.08222	0.03607	-0.02590	0.01516	-0.01289	0.05546
C9	0.44680	0.77652	0.44851	1.00000	0.02769	0.02432	0.04186	0.00340	0.01423	0.00608	0.03074
O9	0.46979	0.82931	0.41709	1.00000	0.06254	0.02045	0.06284	0.00971	0.03632	0.00092	0.04479
Fe4	0.40992	0.69455	0.50694	1.00000	0.02186	0.01860	0.02527	-0.00033	0.01019	0.00161	0.02139
C10	0.53847	0.44124	0.13249	1.00000	0.03399	0.03587	0.02447	-0.00068	0.01135	0.00687	0.03115
O10	0.47927	0.42166	0.04190	1.00000	0.03388	0.06423	0.03923	-0.01374	0.00404	-0.01030	0.04811
C11	0.72154	0.53377	0.20528	1.00000	0.01989	0.03554	0.03495	0.00808	0.00913	0.00178	0.03025
O11	0.77459	0.57094	0.16740	1.00000	0.03658	0.05722	0.05182	0.01837	0.01993	-0.00209	0.04735
C12	0.72741	0.39420	0.27770	1.00000	0.03906	0.03111	0.03291	-0.00213	0.01795	-0.00462	0.03293
O12	0.77725	0.34128	0.27743	1.00000	0.04547	0.03216	0.04665	-0.00493	0.01964	0.01177	0.04049

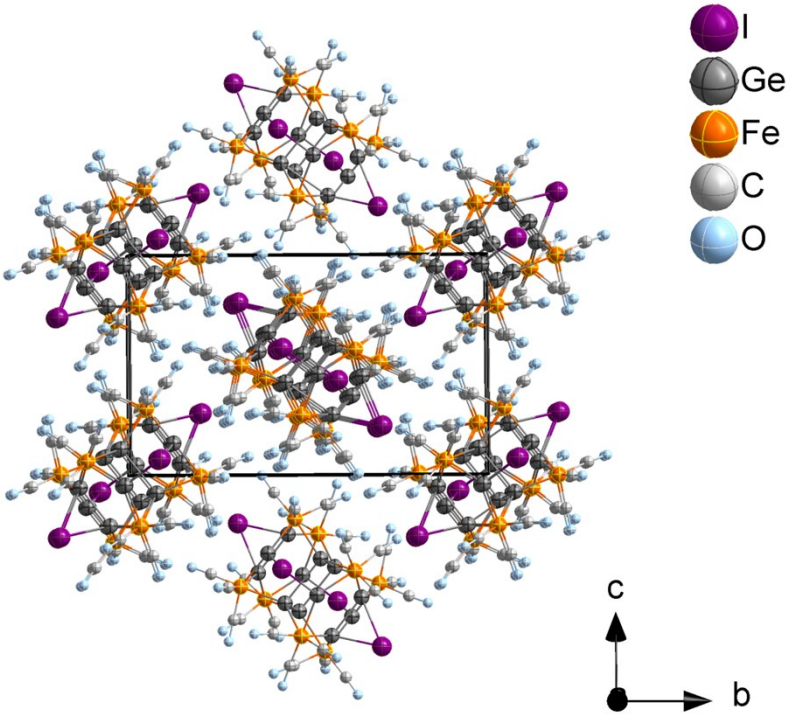

Figure S1. Unit cell of$Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$ crystallizing in the monoclinic space group $P2_1/n$ with 2 formula units per unit cell.

To evaluate the nature of the Ge–Fe bonds, $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$ was compared with $[Fe(CO)_3(GeH_2)_3]^{2+}$ and $[Fe(CO)_3(GeH_3)_3]^-$ (Figure S2). This comparison shows that the single Ge atoms compare well with the Ge atoms in $[Fe(CO)_3(GeH_2)_3]^{2+}$, whereas the Ge_2 pairs fit to the Ge atom in $[Fe(CO)_3(GeH_3)_3]^-$ (Table S3). The higher Mulliken charge of the isolated Ge atoms as well as of the Ge atom in $[Fe(CO)_3(GeH_2)_3]^{2+}$ results in a shorter Ge–Fe distance compared to the Ge_2 pairs in $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$ as well as for the Ge atom in $[Fe(CO)_3(GeH_3)_3]^-$. Both exhibit a lower Mulliken charge and a longer Ge–Fe distance in comparison to the title compound. The higher Mulliken charge is related to a higher valence state of the single Ge atoms compared to the Ge_2 pairs and the Ge atoms in the Ge_4 rectangle. Hence, the shorter distance between the single Ge atoms and Fe can be related to a higher valence state of these Ge atoms. Moreover, it must be noted that there is no evidence for any type of double-bond character according to DFT calculations.

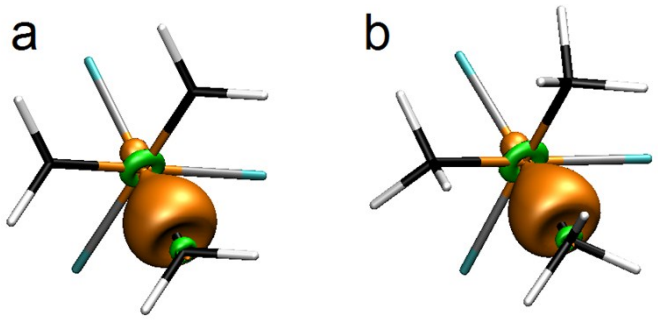

Figure S2. Molecular orbitals of the Fe–Ge bonds in $[Fe(CO)_3(GeH_2)_3]^{2+}$ (a) and $[Fe(CO)_3(GeH_3)_3]^-$ (b).

Table S3. Comparison of the single Ge atoms and the Ge_2 pairs in $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$ with $[Fe(CO)_3(GeH_2)_3]^{2+}$ and $[Fe(CO)_3(GeH_3)_3]^-$.

Compound	**Fe–Ge bond length (pm)**	**Mulliken charge *q*(Fe)(*e*)**	**Mulliken charge *q*(Ge)(*e*)**
$[Fe(CO)_3(GeH_2)_3]^{2+}$	232.3	–1.08	+0.46
$[Fe(CO)_3(GeH_3)_3]^-$	240.1	–1.00	+0.21
$Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$ single Ge atom	230.1(1)-234.5(1)	−0.97	0.335/0.378
$Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$ Ge_2 pair	238.3(1)-243.2(1)	−0.97	0.118

*Fourier-transformed infrared (FT-IR) spectroscopy:*Fourier-transformed infraredspectra were recorded on a Bruker Vertex 70 FT-IR spectrometer (Bruker). The samples were measured as pellets in KBr. Thus, 300 mg of dried KBr and 1 mg of the sample were carefully pestled together and pressed to a thin pellet inside of a glove box. The samples were then transferred in Argon to the spectrometer, and thereafter measured immediately under nitrogen flux.

A comparison of the observed CO vibrations of $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$with selected references is shown in Table S3 and discussed in the main text.

Table S4. Comparison of the CO vibrations of $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$with selected references.

Compound	**Vibration /cm^{-1}**
$Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$	2054, 2014
$(GeI_3)_2Fe(CO)_4$ (hexane solution)[6]	2076
$Fe(CO)_5$[7]	2022, 2000
$Fe_2(CO)_9$[8]	2084, 2028, 1994, 1935

DFT Calculations: The equilibrium geometry of the $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$cluster was optimized by means of a density-functional-theory (DFT) calculation using the PBEh-3c exchange-correlation functional (including the geometrical counterpoise correction and the "D3" dispersion correction with Becke-Johnson damping and three-body terms)[9] and the def2-SVP basis set[10] of Gaussian-type atomic orbitals (this includes an effective core potential for iodine representing 28 core electrons).[11] The TURBOMOLE program package was used for all of the calculations.[12]

During the geometry optimization, the convergence threshold for the energy was set to $10^{-7}\,E_h$and the corresponding threshold for the nuclear gradient to $10^{-4}\,E_h/a_0$(the energy threshold in the self-consistent-field calculations was $10^{-8}\,E_h$). TURBOMOLE's grid 4 was used and its derivatives were taken into account when computing the analytical nuclear gradients. The optimized equilibrium geometry exhibited C_{2h}point-group symmetry (Figure S3a, Figure S4a), and harmonic vibrational frequencies were computed to verify that this geometry represents a minimum on the potential energy hypersurface.At the same level of computation, we have also optimized the $[Ge_{12}\{Fe(CO)_3\}_8]^{4+}$ cluster. Its equilibrium geometry exhibited D_{2h}point-group symmetry (Figure S3b, Figure S4b).

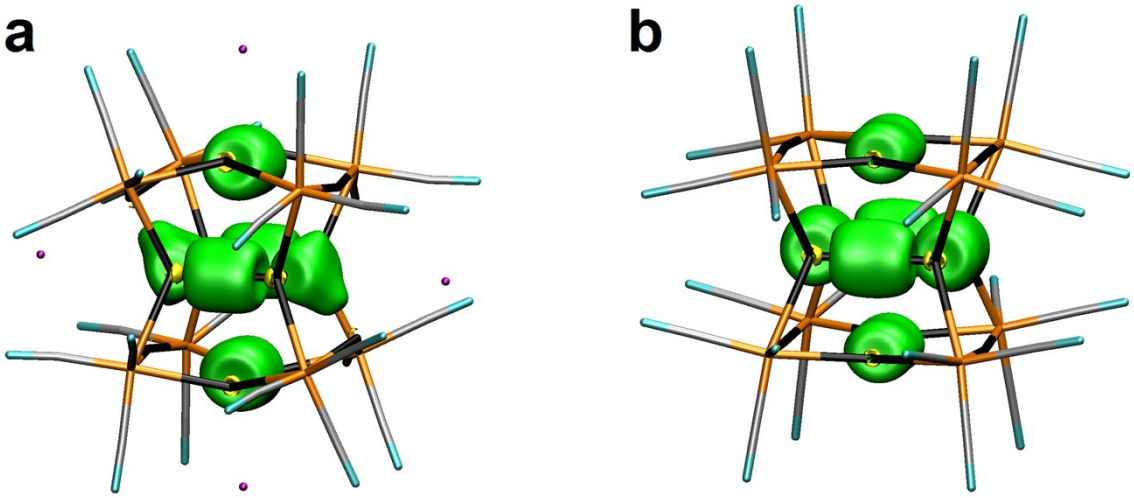

Figure S3. Localized Ge–Ge bonds in the $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$(a)and $[Ge_{12}\{Fe(CO)_3\}_8]^{4+}$ (b)clusters in an approximate octahedral arrangement.

Concerning atomic charges, we have two options: Firstly, we may formally adopt zero charge on iron, $Fe^{\pm0}$. Then, the Ge core can roughly be described by adopting a formal charge of $Ge^{\pm0}$ for the eight Ge atoms that do form Ge–Ge bonds and a formal charge of Ge^{+} for the four atoms that do not. Secondly, we may we adopt a formal negative charge on iron, Fe^{-}.Then, the Ge core can roughly be described by adopting atomic charges of $Ge^{\pm0}$ (4 atoms), Ge^{+} (4 atoms) and Ge^{2+} (4 atoms). This is in very good agreement with the Mulliken charges that were computed for these three different types of atoms (Table S5, Figure S4).

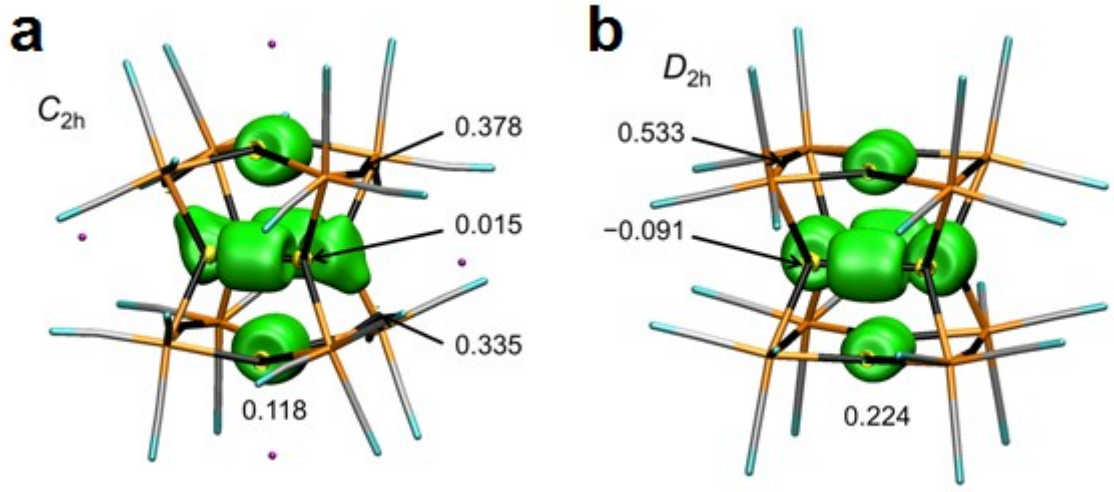

Figure S4.Mulliken charges (*e*) of the $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$(a) and $[Ge_{12}\{Fe(CO)_3\}_8]^{4+}$(b) clusters.

Table S5. Mulliken charges (*e*) in the $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$and $[Ge_{12}\{Fe(CO)_3\}_8]^{4+}$ clusters.

	Fe(−)	Ge(0)	Ge(+)	Ge(2+)
$Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$	−0.967/−0.968	0.015	0.118	0.335/0.378
$[Ge_{12}\{Fe(CO)_3\}_8]^{4+}$	−0.923	−0.091	0.224	0.533

Hence, it is safe to conclude that the Ge_{12} core in the $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$cluster is composed of three different types of Ge atoms, with approximate net charges of 0, 1+ and 2+. These three types are in agreement with the localized two-electron-two-center bonds that the Ge atoms form with four, three and two neighbours, respectively.Hund's localization criterion is obeyed for all atoms in the cluster.[13]

Finally, few selected Ge–Ge distances are shown in Table S6 and Figure S5.

Table S7 and Table S8, finally, show the cartesian coordinates of the $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$and $[Ge_{12}\{Fe(CO)_3\}_8]^{4+}$ clusters as optimized at thePBEh-3c/def2-SVP level.

Table S6. Comparison of the $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$ cluster with related compounds.

Compound	Fe–C bond length (pm)	C–O bond length (pm)	Mulliken charge *q*(Fe)(*e*)	Harmonic vibrational wavenumber (cm^{-1})
$Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$	176.7−177.8	112.9−113.3	−0.97	2201−2295
$[Ge_{12}\{Fe(CO)_3\}_8]^{4+}$	181.3−181.7	111.8−112.1	−0.92	2298−2372
$[Fe(CO)_3(GeH_3)_3]^-$	174.6	114.2	−1.00	2083−2208
$Fe(CO)_5$	178.5−180.4	112.8−113.3	−0.84	2213−2320

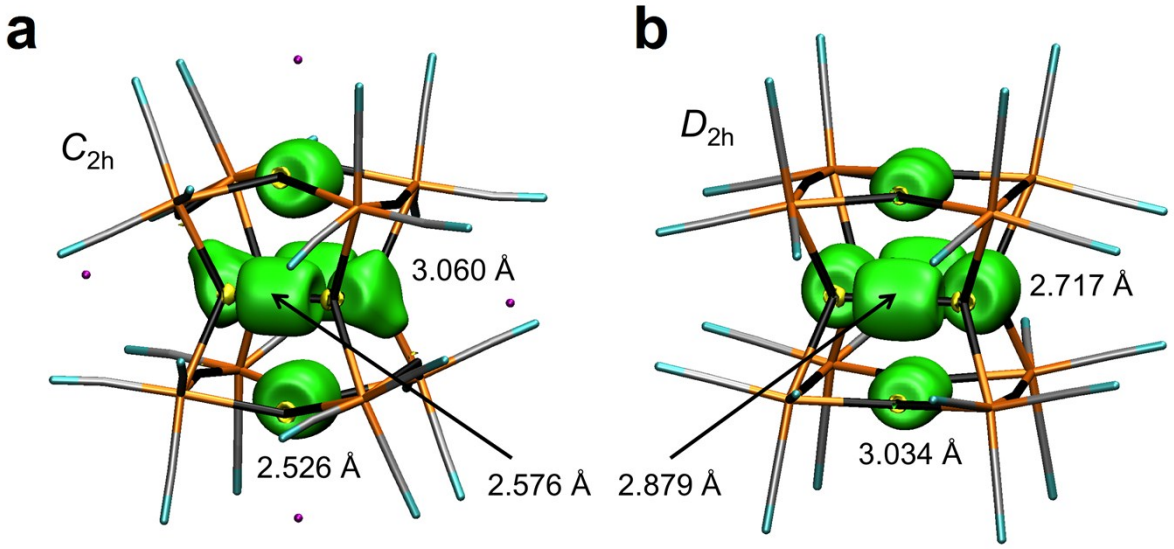

Figure S5. Ge–Ge distances (pm) of the $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$(a) and $[Ge_{12}\{Fe(CO)_3\}_8]^{4+}$(b) clusters.

Table S7. Cartesian coordinates (in Å) of the $Ge_{12}\{Fe(CO)_3\}_8(\mu\text{-}I)_4$cluster, as optimized at the PBEh-3c/def2-SVP level.

I	-0.2317260	-5.2152762	0.0000000
I	-5.0049410	0.3643344	0.0000000
Ge	-0.0525183	-2.6985352	1.2627503
Ge	-1.2861901	0.0688199	1.5302467
Ge	1.2861901	-0.0688199	1.5302467
Ge	2.7448152	-1.6983165	0.0000000
Ge	-2.4409600	-1.9031717	-0.0000000
Ge	-0.0525183	-2.6985352	-1.2627503
Fe	2.1863936	2.0960579	2.2425509
Fe	2.1026709	-2.2711661	2.1693794
O	4.9829467	1.6852167	2.8964120
O	1.3524360	1.0838678	4.8264404
O	2.5337686	4.9149924	2.8254829
O	4.4792362	-1.2502219	3.4901026
O	0.9712552	-2.8353973	4.7781636
C	2.6909751	-3.9126278	1.8833495
C	3.8955432	1.7627867	2.6019509
C	1.6199580	1.5152468	3.8137368
C	2.3830509	3.8251620	2.5624583
C	3.5709316	-1.6170209	2.9279136
C	1.3662409	-2.5598955	3.7546749
O	3.0924633	-4.9581252	1.7258404
I	0.2317260	5.2152762	0.0000000
I	5.0049410	-0.3643344	0.0000000
Ge	0.0525183	2.6985352	1.2627503
Ge	0.0525183	2.6985352	-1.2627503

Ge	-1.2861901	0.0688199	-1.5302467
Ge	1.2861901	-0.0688199	-1.5302467
Ge	-2.7448152	1.6983165	0.0000000
Ge	2.4409600	1.9031717	0.0000000
Fe	-2.1863936	-2.0960579	2.2425509
Fe	2.1863936	2.0960579	-2.2425509
Fe	-2.1863936	-2.0960579	-2.2425509
Fe	-2.1026709	2.2711661	2.1693794
Fe	2.1026709	-2.2711661	-2.1693794
Fe	-2.1026709	2.2711661	-2.1693794
O	-4.9829467	-1.6852167	2.8964120
O	4.9829467	1.6852167	-2.8964120
O	-4.9829467	-1.6852167	-2.8964120
O	-1.3524360	-1.0838678	4.8264404
O	1.3524360	1.0838678	-4.8264404
O	-1.3524360	-1.0838678	-4.8264404
O	-2.5337686	-4.9149924	2.8254829
O	2.5337686	4.9149924	-2.8254829
O	-2.5337686	-4.9149924	-2.8254829
O	-4.4792362	1.2502219	3.4901026
O	4.4792362	-1.2502219	-3.4901026
O	-4.4792362	1.2502219	-3.4901026
O	-0.9712552	2.8353973	4.7781636
O	0.9712552	-2.8353973	-4.7781636
O	-0.9712552	2.8353973	-4.7781636
C	-2.6909751	3.9126278	1.8833495
C	2.6909751	-3.9126278	-1.8833495
C	-2.6909751	3.9126278	-1.8833495
C	-3.8955432	-1.7627867	2.6019509
C	3.8955432	1.7627867	-2.6019509
C	-3.8955432	-1.7627867	-2.6019509
C	-1.6199580	-1.5152468	3.8137368
C	1.6199580	1.5152468	-3.8137368
C	-1.6199580	-1.5152468	-3.8137368
C	-2.3830509	-3.8251620	2.5624583
C	2.3830509	3.8251620	-2.5624583
C	-2.3830509	-3.8251620	-2.5624583
C	-3.5709316	1.6170209	2.9279136
C	3.5709316	-1.6170209	-2.9279136
C	-3.5709316	1.6170209	-2.9279136
C	-1.3662409	2.5598955	3.7546749
C	1.3662409	-2.5598955	-3.7546749
C	-1.3662409	2.5598955	-3.7546749
O	-3.0924633	4.9581252	1.7258404
O	3.0924633	-4.9581252	-1.7258404
O	-3.0924633	4.9581252	-1.7258404

Table S8. Cartesian coordinates (in Å) of the $[Ge_{12}\{Fe(CO)_3\}_8]^{4+}$ cluster, as optimized at the PBEh-3c/def2-SVP level

Ge	1.5170592	0.0000000	-2.3469906
Ge	1.3587412	-1.4396278	0.0000000
Ge	1.3587412	1.4396278	0.0000000
Ge	-0.0000000	2.3235955	-2.3196108
Ge	-0.0000000	-2.3235955	-2.3196108
Ge	-1.5170592	0.0000000	-2.3469906
Fe	2.2516444	2.2204319	2.1976496
Fe	2.2516444	2.2204319	-2.1976496
O	2.5665036	5.0550842	1.5143870
O	5.0278800	1.5193886	1.5568258
O	2.7977502	2.6097973	5.0555636
O	2.5665036	5.0550842	-1.5143870
O	5.0278800	1.5193886	-1.5568258
C	2.5879995	2.4668401	-3.9666416
C	2.4484869	3.9687630	1.7601070
C	3.9634483	1.7718340	1.7994392
C	2.5879995	2.4668401	3.9666416
C	2.4484869	3.9687630	-1.7601070
C	3.9634483	1.7718340	-1.7994392
O	2.7977502	2.6097973	-5.0555636
Ge	1.5170592	0.0000000	2.3469906
Ge	-1.5170592	0.0000000	2.3469906
Ge	-1.3587412	-1.4396278	0.0000000
Ge	-1.3587412	1.4396278	0.0000000
Ge	-0.0000000	-2.3235955	2.3196108
Ge	-0.0000000	2.3235955	2.3196108
Fe	2.2516444	-2.2204319	-2.1976496
Fe	-2.2516444	2.2204319	2.1976496
Fe	-2.2516444	-2.2204319	-2.1976496
Fe	2.2516444	-2.2204319	2.1976496
Fe	-2.2516444	2.2204319	-2.1976496
Fe	-2.2516444	-2.2204319	2.1976496
O	2.5665036	-5.0550842	-1.5143870
O	-2.5665036	5.0550842	1.5143870
O	-2.5665036	-5.0550842	-1.5143870
O	5.0278800	-1.5193886	-1.5568258
O	-5.0278800	1.5193886	1.5568258
O	-5.0278800	-1.5193886	-1.5568258
O	2.7977502	-2.6097973	-5.0555636
O	-2.7977502	2.6097973	5.0555636
O	-2.7977502	-2.6097973	-5.0555636
O	2.5665036	-5.0550842	1.5143870
O	-2.5665036	5.0550842	-1.5143870
O	-2.5665036	-5.0550842	1.5143870
O	5.0278800	-1.5193886	1.5568258
O	-5.0278800	1.5193886	-1.5568258
O	-5.0278800	-1.5193886	1.5568258
C	2.5879995	-2.4668401	3.9666416

C	-2.5879995	2.4668401	-3.9666416
C	-2.5879995	-2.4668401	3.9666416
C	2.4484869	-3.9687630	-1.7601070
C	-2.4484869	3.9687630	1.7601070
C	-2.4484869	-3.9687630	-1.7601070
C	3.9634483	-1.7718340	-1.7994392
C	-3.9634483	1.7718340	1.7994392
C	-3.9634483	-1.7718340	-1.7994392
C	2.5879995	-2.4668401	-3.9666416
C	-2.5879995	2.4668401	3.9666416
C	-2.5879995	-2.4668401	-3.9666416
C	2.4484869	-3.9687630	1.7601070
C	-2.4484869	3.9687630	-1.7601070
C	-2.4484869	-3.9687630	1.7601070
C	3.9634483	-1.7718340	1.7994392
C	-3.9634483	1.7718340	-1.7994392
C	-3.9634483	-1.7718340	1.7994392
O	2.7977502	-2.6097973	5.0555636
O	-2.7977502	2.6097973	-5.0555636
O	-2.7977502	-2.6097973	5.0555636

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