Supporting Information

$[Ge_9\{M(CO)_5\}_3]^{4-}$: Electrophilic Addition of $M(CO)_5$ and $[E_9]^{4-}$ Zintl aions (M = Cr, Mo, W)

Lulu Wang, [a,b] Yi Wang, [a] Zhenyu Li,[a,b] Huapeng Ruan[a,b] and Li Xu*[a]

a. Department State Key Laboratory of Structural Chemistry, Institution Fujian Institute of Research on the Structure of Matter Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China.

b. University of the Chinese Academy of Science, Beijing,100049, P.R. China

E-mail: xli@fjirsm.ac.cn.

Additional experimental details

All manipulations were carried out under argon using standard Schlen-line and glovebox techniques. Ethylenediamine (Acros, 99 %) was distilled over sodium metal and stored in a gastight Schlenk under argon in the glovebox. 18-crown-6 (1, 4, 7, 10, 13, 16- hexaoxa - cyclooctadecane, Alfa-Aesar, 99 %) was dried by refluxing over sodium metal in diethylether and recrystallized from dry n-hexanes. Toluene were dryed with potassium-sodium alloy and then stored in the glovebox.$Cr(CO)_6$ (ACROS, 99%),$Mo(CO)_6$(Alfa-Aesar, 98%),$W(CO)_6$(Alfa-Aesar, 97%)was used as received.Precursors with nominal compositions K_4Ge_9 was synthesized by heating the corresponding mixtures of elements (K :+99 %; Ge: 99.999 %, all from Strem) at 900℃ for two days in sealed niobium containers that were jacketed in evacuated fused-silica ampoules. IR data were recorded as KBr pellets in Nujol mulls on a Magna 750 FT-IR spectrometer photometer. Electrospray mass spectra were recorded from DMF solutions of **1** with nitrogen as sheath gas flow on a Finnigan LCQ-Ion Trap Mass Spectrometer (LCQ DECAX-30000 LCQ Deca XP) in negative-ion mode (spray voltage 4.5kV, capillary temperature 275℃capillary voltage 15V). The samples were made up inside a glovebox under an inert atmosphere and rapidly transferred to the spectrometer in an air-tight syringe by direct infusion with a Harvard syringe pump at 15 $mLmin^{-1}$.

Synthesis and Crystallization of $[K(18\text{-crown-6})]_4\{Ge_9[Cr(CO)_5]_3\}$;K_4Ge_9 (114mg, 0.141mmol) and18-crown-6 (151mg, 0.571mmol) were dissolved in 2ml ethylenediamine and stirred for 10 minutes at room temperature resulting in a dark red solution. $Cr(CO)_6$ (18.1mg , 0.0821 mmol) was then added, and the mixture is stirred for another 30 minutes to an hour at room temperature, upon which it turns brownish-green. The temperature is then raised to 60℃ and kept for 2 hours. The resulting dark brownish solution is centrifuged and filtered via a glass fiber pipette. Aliquots of this solution are used for crystallization by layering with toluene (8 ml) solutions. The solution afforded long black needlelike crystals $[K(18\text{-crown-6})]_4\{Ge_9[Cr(CO)_5]_3\}$(yield of 20-30% based on the crown ether) after several days to a week. The IR spectrum (KBr) of **1** shows the characteristic CO stretching vibrations: 1990cm^{-1} (vs, sh), 1882cm^{-1}(vs, sh).

Synthesis and Crystallization of $[K(18\text{-crown-6})]_4\{Ge_9[Mo(CO)_5]_3\}$;K_4Ge_9 (114mg, 0.141 mmol) and 18-crown-6 (151mg, 0.571mmol) were dissolved in 2ml ethylenediamine and stirred for 10 minutes at room temperature resulting in a dark red solution. $Mo(CO)_6$ (21.7mg , 0.0821 mmol)was then added,and the mixture is stirred for another 30 minutes to an hour at room temperature, upon which it turns brownish-green. The temperature is then raised to 60℃ and kept for 2 hours. The resulting dark brownish solution is centrifuged and filtered via a glass fiber pipette. Aliquots of this solution are used for crystallization by layering with toluene (8 ml) solutions. The solution afforded long black needlelike crystals $[K(18\text{-crown-6})]_4\{Ge_9[Mo(CO)_5]_3\}$(yield of 20-30% based on the crown ether) after several days to a week. The IR spectrum (KBr) of **1** shows the characteristic CO stretching vibrations: 2025cm^{-1} (s, sh), 1901cm^{-1}(vs, broad).

Synthesis and Crystallization of $[K(18\text{-crown-6})]_4\{Ge_9[W(CO)_5]_3\}$;$K_4Ge_9$ (114mg, 0.141mmol) and 18-crown-6 (151mg, 0.571mmol) were dissolved in 2ml ethylenediamine and stirred for 10 minutes at room temperature resulting in a dark red solution.W(CO)6(28.9mg,0.0821mmol) was then added, and the mixture is stirred for another 30 minutes to an hour at room temperature, upon which it turns brownish-green. The temperature is then raised to 60℃ and kept for 2 hours. The resulting dark brownish solution is centrifuged and filtered via a glass fiber pipette. Aliquots of this solution are used for crystallization by layering with toluene (8 ml) solutions. The solution afforded long black needle-like crystals $[K(18\text{-crown-6})]_4\{Ge_9[W(CO)_5]_3\}$(yield of 20-30% based on the crown ether) after several days to a week.. The IR spectrum (KBr) of **1** shows the characteristic CO stretching vibrations: 2046cm^{-1} (s, sh) , 1921cm^{-1}(vs, sh).

Structure Determination Data sets were collected on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo Ka radiation (λ= 0.71073 Å) at 173 K. The crystals were selected under mixed Araldite resin,mounted on fibers .The structure was solved by direct methods and refined on F^2 using the SHELXTL V6.21 package.[1]

DFT Calculation Computational studies on the discrete clusters $[Ge_9\{W(CO)_5\}_3]^{4-}$were carried out using the GAUSSIAN 09 program package (Revision A.02).[2] Hybrid DFT calculations were performed with the B3LYP functional.[3,4] GAUSSVIEW [5]was used to visualize molecular orbitals. In these calculations, the solvent effects were taken into account by the Polarizable Contiuum Model (PCM)[6].

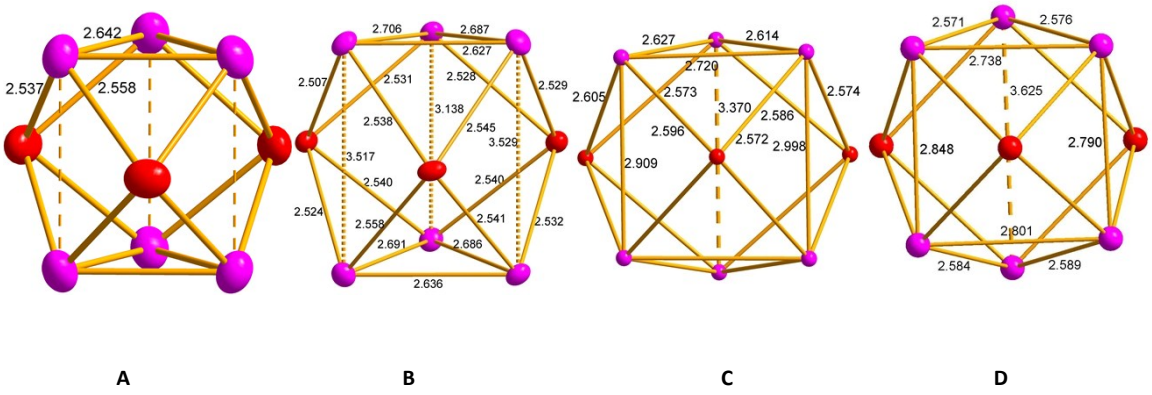

Fig. S1. Structural comparisons of 22e-$[Ge_9]$ in (**A**) D_{3h}-**3a**, (**B**) distorted D_{3h}-$[Ge_9\{Si(SiMe_3)_3\}_3]^{-}$ [20a], (**C**) C_{4v}-$Cs_4Ge_9(en)$,[16] and (**D**) C_{2v}-[K-(2,2)diaza-18-crown-6]$K_3Ge_9(en)_2$.[19]

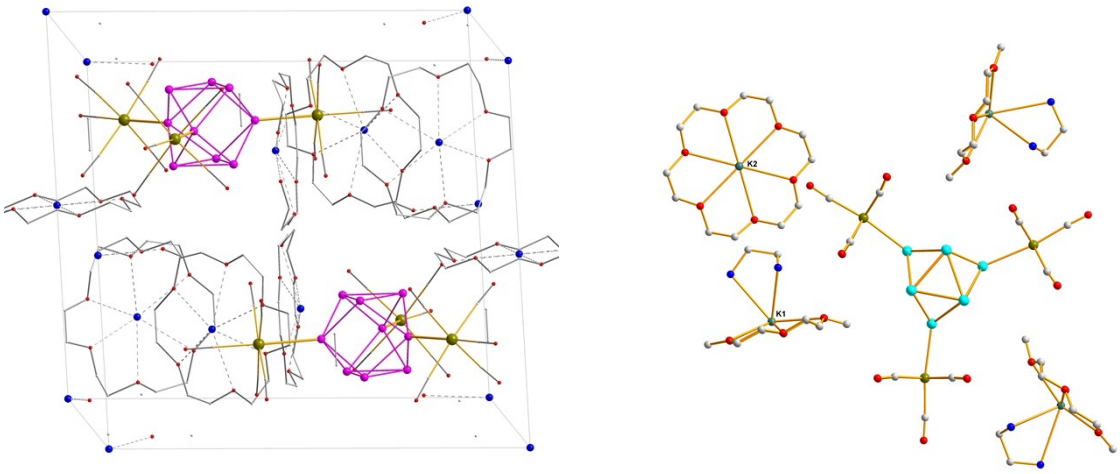

Fig. S2. Side-directed arrangement of $[K(18\text{-crown-}6)]^+$ counterions toward the $[Ge_9]^{4-}$ core cluster of **3**.

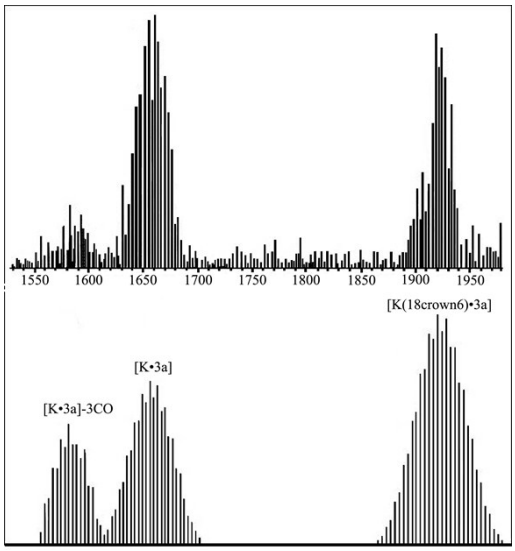

Fig. S3. The observed (top) and theoretical (bottom) electrospray mass spectra in negative ion mode of the crystalline **3** in DMF solution (all species are monoanions). The dianion $[Ge_9\{W(CO)_5\}_3]^{2-}$ coupled with K^+ or $[K(18\text{-crown-6})]^+$ is clearly visible .

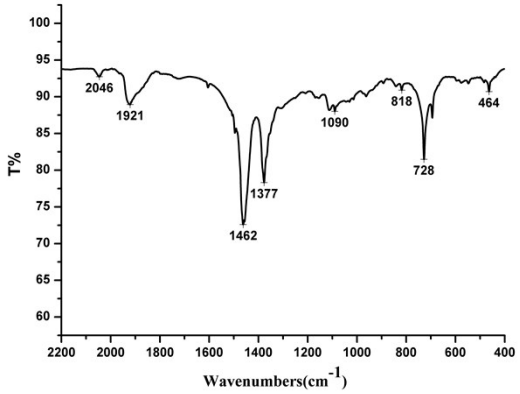

Fig. S4. IR spectrum of **3** in Nujol mulls.

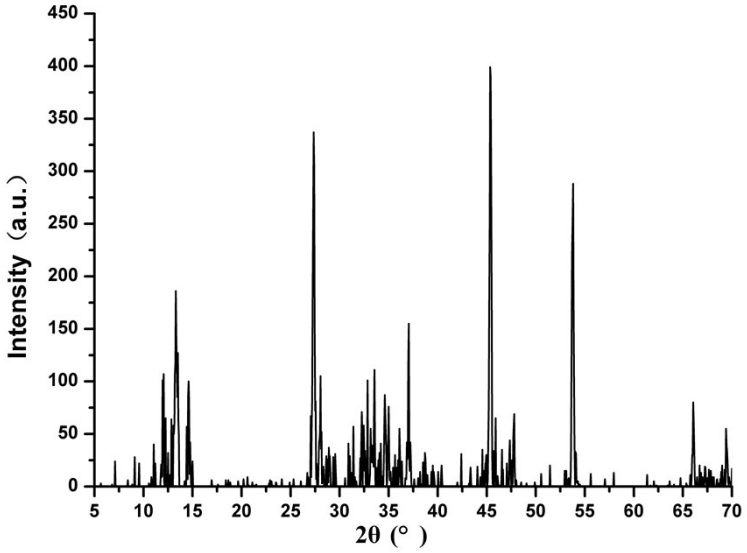

Fig. S5. PXRD of the precursor with a nominal composition "K_4Ge_9".

References

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