Supporting Information

$\{Ge_8([Mo(CO)_3])_2\}^{4-}$: 20-Electron Empty Ten-vertex Zintl Anions with Two Vertices Replaced by Transition Metals

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Experimental Section

All manipulations were carried out under argon using standard Schlenk-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-hexaoxacyclooctadecane, Alfa-Aesar, 99 %) was dried by refluxing over sodium metal in diethylether and recrystallized from dry n-hexanes. Toluene was dried with potassium-sodium alloy and then stored in the glovebox. Mo(CO)6(Alfa-Aesar, 98%) was used as received. Precursors(its composition can not be clearly identified.) with nominal composition K4Ge9 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.

$[K(18\text{-crown-6})]_3K[Ge_8(Mo(CO)_3)_2]$•en(**1**): The binary alloy with the nominal composition "K_4Ge_9"(114 mg, 0.141 mmol) and 18-crown-6(151 mg, 0.571 mmol) were dissolved in 2 mL ethylenediamine (en) and stirred for 10 minutes at room temperature, resulting in a dark red solution, to which $Mo(CO)_6$(21.7 mg, 0.0821 mmol) was added. The resulting solution was stirred for 30 minutes at room temperature and turned brownish-green. The temperature was then raised to 60℃ and kept for about 4 hours. The resulting dark brownish green solution was filtered and the filtrate was layered with toluene (8 ml). Red, transparent thin plate crystals of 1 were obtained after one week (yield, ca. 30 % based on "K_4Ge_9"). The IR spectrum (KBr) of **1** shows the characteristic CO stretching vibrations: 2034, 1936, 1882 and 1852 cm-1.

The quantitative energy-dispersive X-ray spectroscopy (EDX, JEOL-SEM, JSM-6700F) analysis of the crystals shows the presence of elements K, Mo, and Ge, with roughly the expected ratios.

DFT calculations were performed using the *GAUSSIAN03* program package (Revision D.02) [27] and crystal structure parameters. All DFT calculations were carried out using the B3LYP functional, that is, Beck's hybrid three-parameter exchange functional [28] with the Lee-Yang-Parr correlation functional.[29] In these calculations, the solvent effects were taken into account by the Polarizable Contiuum Model.[30]

Reference

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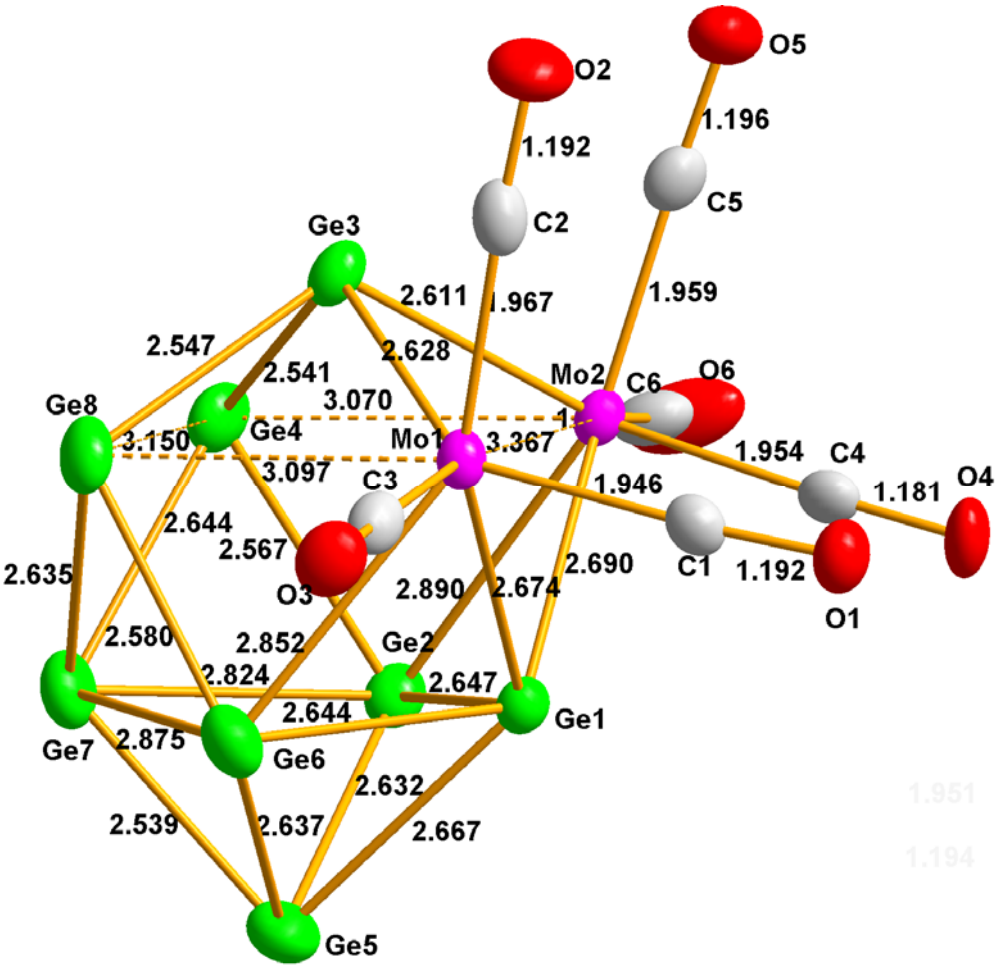

Fig. S1 ORTEP drawing of 20e-$[Ge_8(Mo(CO)_3)_2]^{4-}$ (**1a**) of with 50% probability ellipsoids.

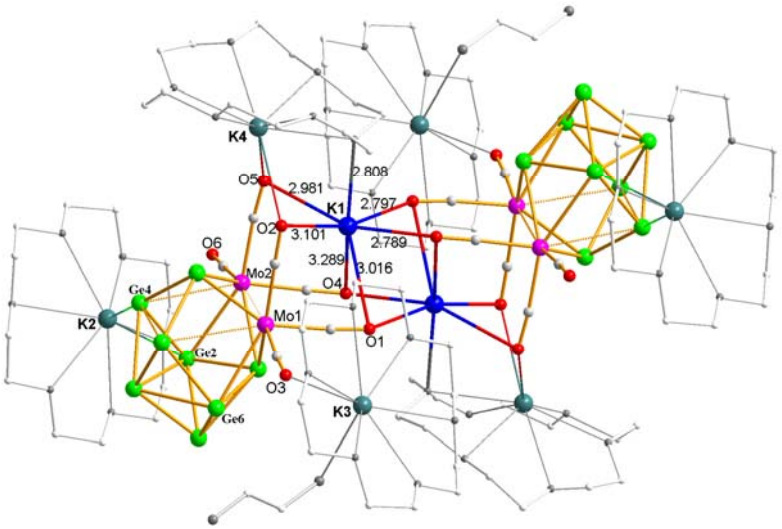

Fig. S2 Crystal structures of **1**.

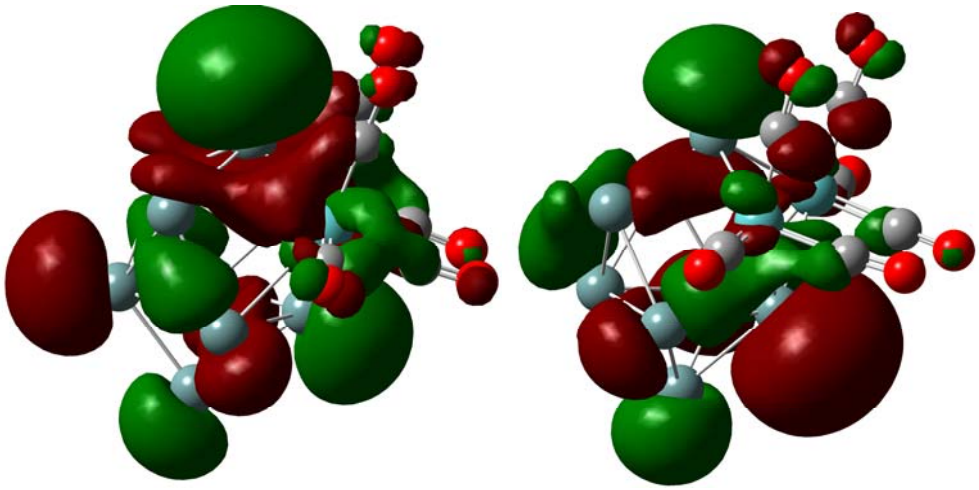

Fig.S3 LUMO of **1a** HOMO of **1a**

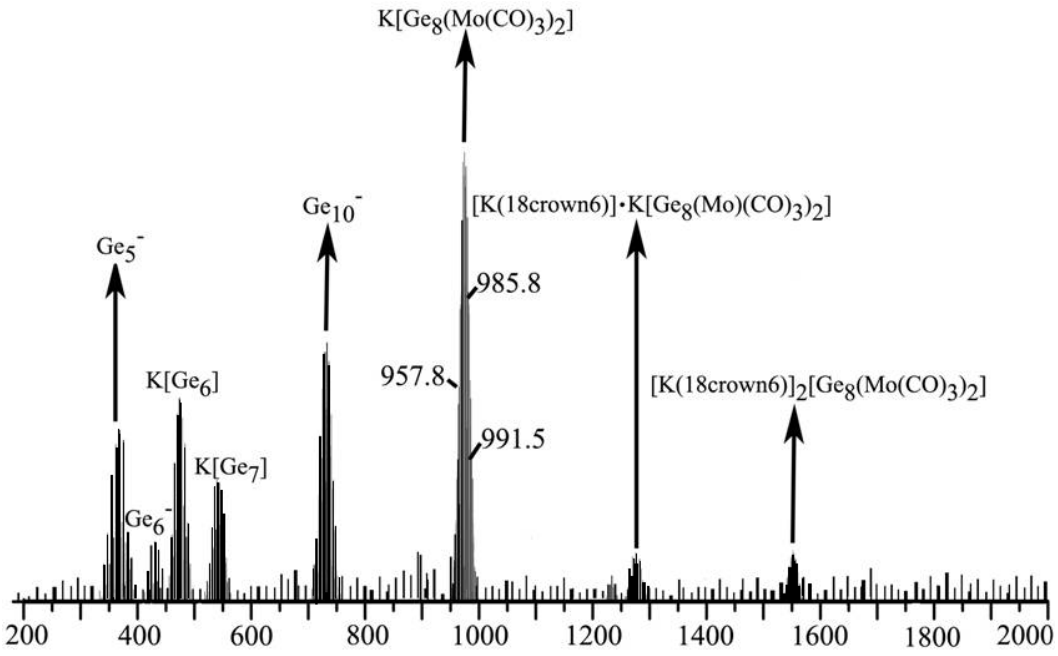

Fig. S4 Electrospray mass spectrum recorded from a DMF solution of **1**.

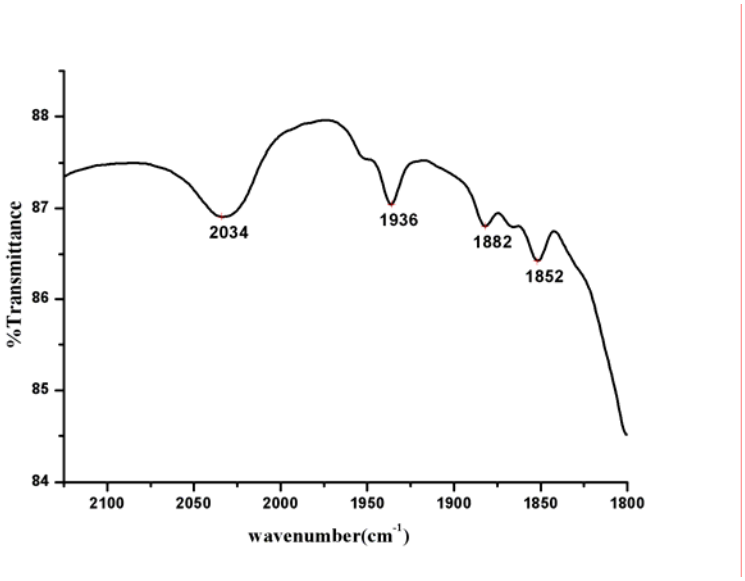

Fig. S5. IR spectrum of **1** in Nujol mulls, which cuts out the absorption of background.

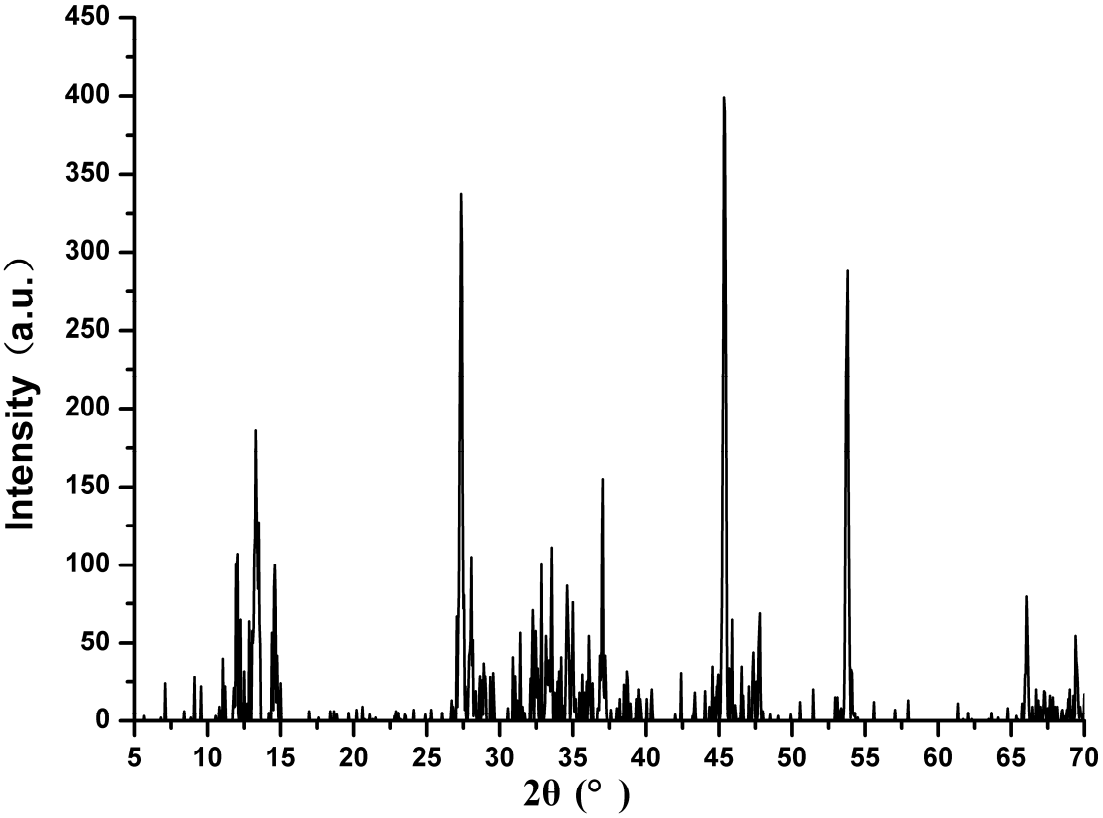

Fig. S6. PXRD of the precursor with a nominal composition "K_4Ge_9".