# Supporting Information

# $[(\eta^3\text{-}Bi_3)_2(IrCO)_6(\mu_4\text{-}Bi)_3]^{3-}$: a new archetype of 15-vertex deltahedral hybrid From $Bi_x^{x-}$-coordination aggregation of cationic $[IrCO]^+$ units

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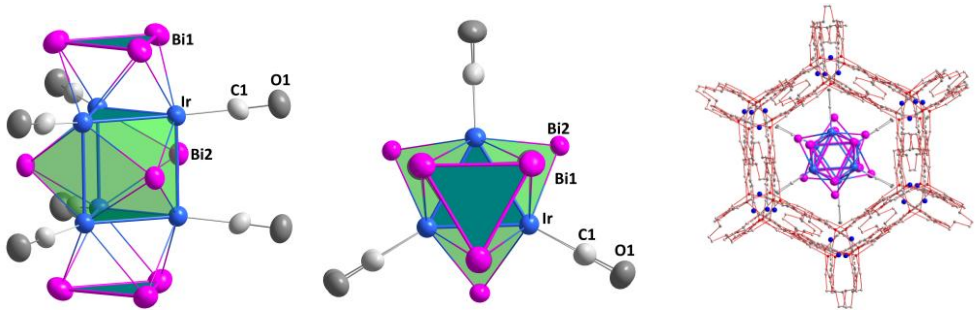
## S1 Experimental Details

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. Toluene was dried with potassium-sodium alloy and then stored in the glovebox. Precursors with nominal composition $K_5Bi_4$[1] was synthesized by heating the corresponding mixtures of elements (K: +99%; Bi: 99.999 %, all from Strem) at 800℃ for two days in sealed niobium containers that were jacketed in evacuated fused-silica ampoules. 2,2,2-cryptand(TCI, 99%) and $Ir(CO)_2(acac)$ (acac = acetylacetonate) (Aladdin, 97%) were used as received. IR data were recorded as KBr pellets in Nujol mulls on a Magna 750 FT-IR spectrometer photometer.

Synthesis of $[K(2,2,2\text{-cryptand})]_3[Bi_3\{Ir_6(CO)_6(\mu_4\text{-}Bi)_3\}Bi_3]$(**1**): The binary alloy with the nominal composition $K_5Bi_4$ ( 89 mg, 0.0863 mmol) and 2,2,2-cryptand(80 mg, 0.212 mmol) were dissolved in 2 mL ethylenediamine and stirred for 0.5 hours at room temperature, resulting in a dark green solution, to which $Ir(CO)_2(acac)$ (9 mg, 0.026 mmol) was added. The resulting solution was stirred for 0.5 hour at room temperature and turned brown-red. The resulting solution was filtered via a glass fiber pipette and the filtrate was layered with toluene (7 ml). Black, needle crystals of 1 were obtained after 15 days (yield, ca. 5% based on Ir). IR ($\nu_{CO}$): 1936 $cm^{-1}$ (KBr pellet)

## S2 Molecular and Crystal structures




**(a)** **(b)** **(c)**

**Fig. S2.1** Crystallographic $D_3$-symmetric molecular structures of 1a with 30% probability thermal ellipsoids viewed down along 2-fold axis (a) and 3-fold axis (b), respectively. The crystal structure (c) of **1** shows the hexagonal channels formed by the packing of $[K\text{-}2,2,2\text{-cryptand}]^+$ in which **1a** is encapsulated.

## S3 Mass spectrum of 1

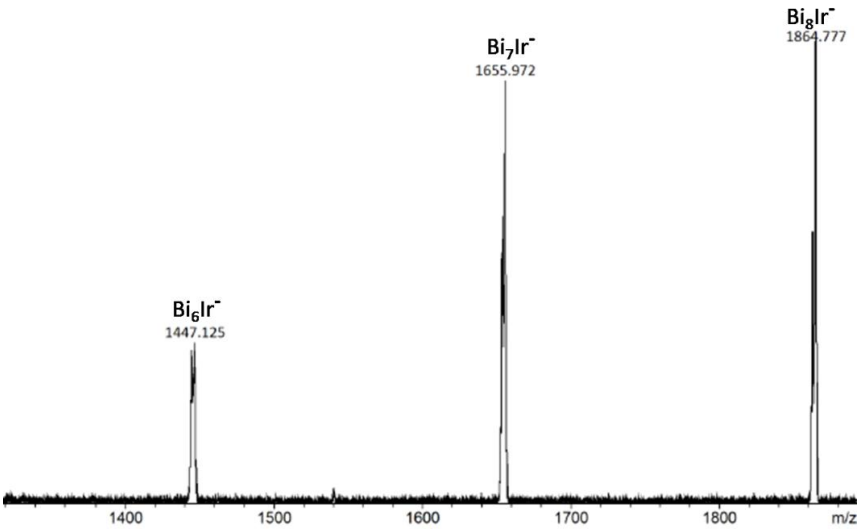
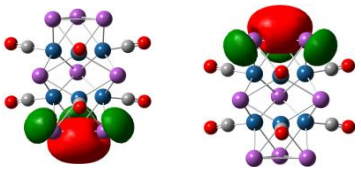


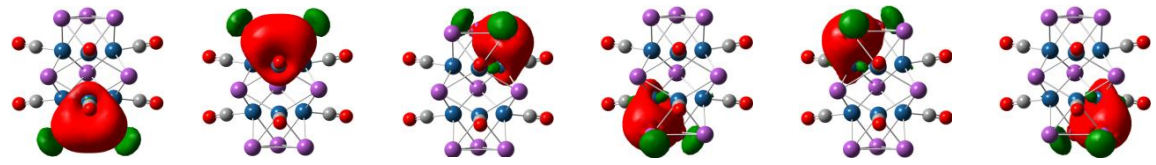

**Fig. S3.1.** LDI-TOF mass spectrum of **1**. LDI-TOF-MS (laser desorption/ionization time-of-flight mass spectrometry) of **1** was recorded on a rapifleX MALDI Tissuetyper (Bruker Daltonics, Germany) in negative-ion mode. As shown in Figure S3.1, **1** was found to lose carbonyl groups and recombine to give $[Bi_xIr]^-$ (x= 6, 7, 8) as in the case of other MS-characterized metal carbonyl clusters.(ref. 3g,8,15c)

## S4 Computational Methods and Details

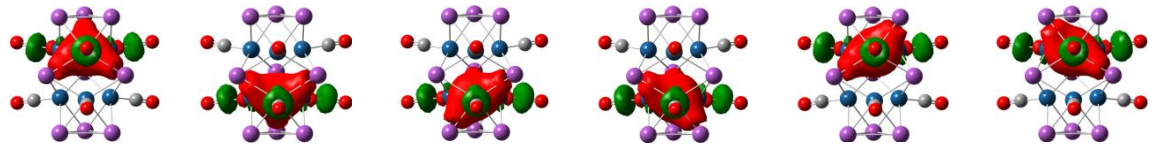
DFT calculations were performed using the GAUSSIAN 09(Revision D.01)[2] program package on the PBE0/def2-TZVP level.[3,4] In these calculations, the solvent effects were taken into account by the conductor-like polarizable contiuum model (C-PCM).[5] The geometric and electronic structure for **1a** was optimized and the final Cartesian coordinates were provided in Table S4.1. The analyses of adaptive natural density portioning (AdNDP) were performed by Multiwfn[6], which is a multifunctional wavefunction analysis program developed by Lu et. al. and can be freely downloaded.



(a) $\eta^3$-$Bi_3$ *3c-2e* bonding in **1a**



(b) $Bi_2Ir$ *3c-2e* bonding



(c) $Ir_3$-based *2e* bonding

**Fig. S4.1** Multi-center *2e*-AdNDP orbitals for **1a** (Bi: purple; Ir: blue; C: grey; O: red)

**Table S4.1** Cartesian Coordinates of optimized **1a**.

| | | | |
|---|---|---|---|
| Ir | -1.51200859 | -0.87295856 | 1.44199600 |
| Bi | -2.38968265 | 1.37968392 | -0.00000000 |
| Bi | 0.00000000 | -2.75936784 | -0.00000000 |
| Bi | -1.58107906 | 0.91283642 | 3.50340000 |
| Bi | 0.00000000 | -1.82567284 | 3.50340000 |
| C | -3.08057069 | -1.77856832 | 1.64692200 |
| Ir | 0.00000000 | 1.74591713 | 1.44199600 |
| Ir | -1.51200859 | -0.87295856 | -1.44199600 |
| Ir | 0.00000000 | 1.74591713 | -1.44199600 |
| Bi | -1.58107906 | 0.91283642 | -3.50340000 |
| Ir | 1.51200859 | -0.87295856 | 1.44199600 |
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| Bi | -0.00000000 | -1.82567284 | -3.50340000 |
| Bi | 1.58107906 | 0.91283642 | 3.50340000 |
| O | -4.08584088 | -2.35896133 | 1.82350800 |
| Bi | 2.38968265 | 1.37968392 | -0.00000000 |
| C | 0.00000000 | 3.55713664 | 1.64692200 |
| C | -3.08057069 | -1.77856832 | -1.64692200 |
| Bi | 1.58107906 | 0.91283642 | -3.50340000 |
| C | -0.00000000 | 3.55713664 | -1.64692200 |
| C | 3.08057069 | -1.77856832 | 1.64692200 |
| C | 3.08057069 | -1.77856832 | -1.64692200 |
| O | 0.00000000 | 4.71792266 | 1.82350800 |
| O | -4.08584088 | -2.35896133 | -1.82350800 |
| O | 0.00000000 | 4.71792266 | -1.82350800 |
| O | 4.08584088 | -2.35896133 | 1.82350800 |
| O | 4.08584088 | -2.35896133 | -1.82350800 |

## S5 Energy Dispersive X-ray (EDX) Spectroscopy

The quantitative Energy-Dispersive X-ray spectroscopy (EDX, JEOL-SEM, JSM-6700F) analysis of the crystals shows the presence of elements Bi, Ir and K with the roughly expected ratios 9/6/3.

| | EDX | | |
|---|---|---|---|
| Element | Weight % | Atom % | Ratio |
| Bi | 59.34 | 49.33 | 9 |
| Ir | 36.73 | 33.20 | 6.05 |
| K | 3.93 | 17.47 | 3.18 |

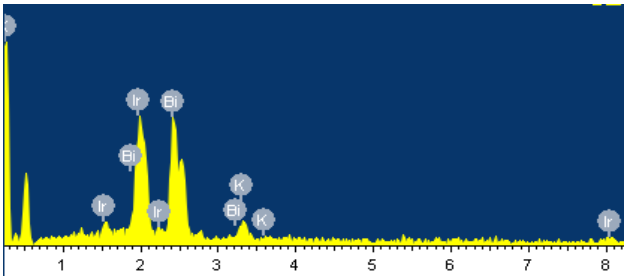


**Fig. S5.1.** EDX spectroscopy of **1**.

## S6 References


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