Supporting Information

Transition-metal-mediated activation of the heptaarsenide trianion: Isolation of a diaryltetraarsenabutadienediide

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CONTENTS:

1. Experimental section

1.1. General synthetic methods. All reactions and product manipulations were carried out under an inert atmosphere using standard Schlenk-line or glovebox techniques (MBraun UNIlab glovebox maintained at < 0.1 ppm H_2O and < 0.1 ppm O_2). The Zintl phase K_3As_7 was synthesised according to a previously reported synthetic procedure from a mixture of the elements (K: 99.95%, Strem; As: 99.99%, Alfa-Aesar).[1] $[Co(mes)_2(PEt_2Ph)_2]$ was prepared following the account reported by Chatt and Shaw.[2] Anhydrous $CoBr_2$ (Co 26.6% min, Alfa Aesar), PEt_2Ph (98%, Alfa Aesar), Mg turnings (Fisher) and 2-bromomesitylene (99%, Alfa Aesar) were used as received. 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; 99+%, Merck) was also used as received after careful drying under vacuum. Toluene (tol; 99.9%, Rathburn), diethylether (Et_2O; pesticide residue grade, Fisher) and dimethylformamide (DMF; 99.9%, Rathburn) were purified using an MBraun SPS-800 solvent system. Ethylenediamine (en; 99%, Aldrich), tetrahydrofuran (THF; 99.9%, Rathburn) and pyridine (py; 99+%, Alfa Aesar) were distilled over sodium metal, a sodium metal/benzophenone mixture and CaH_2, respectively. d_5-Pyridine (99.5%, Cambridge Isotope Laboratories, Inc.) was dried over CaH_2 and vacuum distilled. All solvents were stored under argon in gas–tight ampoules. In addition toluene, diethylether and THF were stored over activated 3 Å molecular sieves (Acros).

Synthesis of $[K(2,2,2\text{-crypt})]_2[Co(\eta^3\text{-}As_3)\{\eta^4\text{-}As_4(mes)_2\}]\cdot py\cdot 0.5tol$: To a solution of K_3As_7 (500 mg, 0.78 mmol) and 2,2,2-crypt (585 mg, 1.56 mmol) in en (10 ml), a solution of $[Co(mes)_2(PEt_2Ph)_2]$ (441 mg, 0.70 mmol) in THF (10 ml) was added and the mixture was left to stir under argon for 3 hours. The resulting solution was reduced to dryness under a dynamic vacuum yielding a dark brown residue which was subsequently washed with Et_2O (30 mL) to remove residual PEt_2Ph. The solid was dried under vacuum for a further 2 hours to give the product as a dark brown solid (785 mg, 61% yield). Crystals of $[K(2,2,2\text{-crypt})]_2[\mathbf{1}]\cdot py\cdot 0.5tol$ suitable for single crystal X-ray diffraction could be grown by allowing a concentrated pyridine solution of the brown solid to diffuse into toluene. Anal. Calcd for $C_{54}H_{94}As_7CoK_2N_2O_{12}$: C, 39.22; H, 5.73; N, 3.39. Found: C, 38.93; H, 5.55; N, 3.18. ^1H NMR (499.93 MHz, d_5-pyridine): δ (ppm) 6.77 (s, 2H, $C_6H_2(CH_3)_3$), 3.38 (br s, 12H, 2,2,2-crypt), 3.32 (t, 12H, 2,2,2-crypt, $^3J_{H–H}$ = 5 Hz), 2.31 (t, 12H, 2,2,2-crypt, $^3J_{H–H}$ = 5 Hz), 2.18 (s, 3H, *para*-CH_3), 2.13 (s, 6H, *ortho*-CH_3). ^{13}C NMR (125.72 MHz, d_5-pyridine): δ (ppm) 154.8 (*ipso*-aryl), 142.8 (*ortho*-aryl), 131.7 (*para*-aryl), 127.6 (*meta*-aryl), 70.9 (2,2,2-crypt), 68.1 (2,2,2-crypt), 54.3 (2,2,2-crypt), 30.7 (*ortho*-CH_3), 21.4 (*para*-CH_3). ESI-MS (–ve ion mode; DMF): *m/z* 702.4 $[CoAs_7(mes)]^-$, 821.8 $[CoAs_7(mes)_2]^-$. ESI-MS (+ve ion mode DMF): *m/z* 1653.7 $\{[K(2,2,2\text{–crypt})]_2[CoAs_7(mes)_2]\}^+$, 2068.2 $\{[K(2,2,2\text{–crypt})]_3[CoAs_7(mes)_2]\}^+$.

1.2. Single crystal X-ray structure determination

Single crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.[3] Data were collected at 150 K using mirror monochromated Cu Kα radiation (λ = 1.5418 Å) and processed using the CrysAlisPro package, including unit cell parameter refinement and inter–frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[4] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro package. The structure was subsequently solved using direct methods, and refined on F^2 using the SHELXL 97-2 package.[5]

$[K(2,2,2\text{-crypt})]_2[Co(\eta^3\text{-}As_3)\{\eta^4\text{-}As_4(mes)_2\}]\cdot py\cdot 0.5tol$: $C_{62.5}H_{103}As_7CoK_2N_5O_{12}$; $M_r = 1778.07$; crystal colour and morphology: thin yellow plates; crystal size: 0.10 × 0.06 × 0.01 mm; triclinic; space group: *P–1*; $a = 13.1075(4)$ Å; $b = 13.6595(4)$ Å; $c = 24.3451(8)$ Å; $\alpha = 78.450(3)°$; $\beta = 84.386(3)°$; $\gamma = 62.288(3)°$; $V = 3780.6(2)$ Å^3; $Z = 2$; T = 150(2) K; $\rho_{calcd} = 1.562$ g cm^{-3}; $\mu = 6.635$ mm^{-1}; 56712 reflections collected; 13342 independent reflections; $R_{int} = 0.1252$; R1 = 6.44 and R2 = 17.36 for $I \geq 2\sigma(I)$; R1 = 8.20 and R2 = 18.45 for all data.

1.3. Additional characterization techniques

Positive and negative ion mode electrospray mass spectra were recorded on DMF solutions (10–20 μM) on a Masslynx LCT Time of Flight mass spectrometer with a Z-spray source (150°C source temperature, 200°C desolvation temperature, 3.2 kV capillary voltage and 25 V cone voltage). The samples were made up inside a glovebox under an inert atmosphere and rapidly transferred to the spectrometer in an air-tight syringe. Samples were introduced directly with a 1 mL SGE syringe and a syringe pump at 0.6 mL h^{-1}.

^{1}H and ^{13}C NMR spectra were acquired at 499.9 and 125.0 MHz, respectively on a Varian Unity-plus 500 NMR spectrometer. ^{1}H and ^{13}C spectra are reported relative to TMS and were referenced to the most downfield residual solvent resonance (d_5-pyridine: δ_H 8.74 ppm, δ_C 150.4 ppm).

Elemental analyses were carried out by Stephen Boyer of the London Metropolitan University. Samples (approx. 5 mg) were submitted in sealed Pyrex ampoules.

2. Computed structures and analysis of electronic structure

2.1 General computational details

All calculations described in this paper were carried out at the DFT level of theory with the Gaussian 03 program.[6] Geometries were fully optimized using the BP86 functional[7] in conjunction with a def-TZVP basis on Co and As[8] and a def-SVP basis on C and H.[9] A polarisable continuum with $\varepsilon = 78.4$ was included in the model to mimic the confining effects of the crystal lattice. C_s symmetry was imposed in all calculations. Topological properties of electronic densities were characterised using the Atoms In Molecules (AIM) theory of Bader with the AIM2000 program.[10,11]

2.2. Optimized computed structure

Table S1: Interatomic distances [Å] and bond angles [°] for the [Co(η^3-As_3){η^4-As_4(mes)$_2$}]$^{2-}$ (**1**) cluster anion crystallographically characterized in [K(2,2,2-crypt)]$_2$[**1**]·py·0.5tol and for the optimized computed structure. Numbering scheme as used in Figure 1.

Distance	**1**	**1_{DFT}**
Co1–As1	2.467(1)	2.49
Co1–As2	2.379(1)	2.41
Co1–As3	2.394(1)	2.41
Co1–As4	2.449(1)	2.49
Co1–As5	2.364(1)	2.40
Co1–As6	2.393(1)	2.44
Co1–As7	2.415(1)	2.44
As1–As2	2.373(1)	2.42
As2–As3	2.395(1)	2.43
As3–As4	2.386(1)	2.42
As5–As6	2.375(1)	2.43
As5–As7	2.381(1)	2.43
As6–As7	2.387(2)	2.42
As1–C1	2.006(6)	2.02
As4–C11	2.019(6)	2.01
As1–As4	3.132(1)	3.23
Angle		
C1–As1–As2	98.44(17)	101.8
As1–As2–As3	97.02(3)	99.5
As2–As3–As4	100.66(3)	99.5
As3–As4–C11	94.70(17)	101.8
As5–As6–As7	60.01(4)	60.2
As6–As7–As5	59.74(4)	60.2
As7–As5–As6	60.26(5)	59.6

Optimised cartesian coordinates [Å] for 1$_{\mathrm{DFT}}$

Atom	x	y	z
Co	0.284423000	-0.582254000	0.000000000
As	-1.078731000	0.736146000	1.613613000
As	-1.535941000	-1.603681000	1.214477000
As	-1.535941000	-1.603681000	-1.214477000
As	-1.078731000	0.736146000	-1.613613000
As	2.615560000	-0.007559000	0.000000000
As	1.870623000	-1.980333000	1.208639000
As	1.870623000	-1.980333000	-1.208639000
C	-0.596930000	0.735152000	-3.569190000
C	-1.463872000	0.217948000	-4.582721000
C	0.569883000	1.453369000	-3.977638000
C	-1.109613000	0.356765000	-5.942923000
C	0.884158000	1.562895000	-5.350872000
C	0.070121000	1.007491000	-6.356415000
H	-1.791999000	-0.053182000	-6.708724000
H	1.795678000	2.114652000	-5.641669000
C	-0.596930000	0.735152000	3.569190000
C	0.569883000	1.453369000	3.977638000
C	-1.463872000	0.217948000	4.582721000
C	0.884158000	1.562895000	5.350872000
C	-1.109613000	0.356765000	5.942923000
C	0.070121000	1.007491000	6.356415000
H	1.795678000	2.114652000	5.641669000
H	-1.791999000	-0.053182000	6.708724000
C	0.444190000	1.100536000	-7.819771000
H	1.170212000	1.918035000	-8.005753000
H	0.914623000	0.157678000	-8.178269000
H	-0.444874000	1.275785000	-8.460926000
C	0.444190000	1.100536000	7.819771000
H	0.914623000	0.157678000	8.178269000
H	1.170212000	1.918035000	8.005753000
H	-0.444874000	1.275785000	8.460926000
C	1.471187000	2.144782000	2.978564000
H	2.329601000	2.634263000	3.481492000
H	1.858627000	1.435811000	2.214813000
H	0.920557000	2.926325000	2.409079000
C	1.471187000	2.144782000	-2.978564000
H	1.858627000	1.435811000	-2.214813000
H	2.329601000	2.634263000	-3.481492000
H	0.920557000	2.926325000	-2.409079000
C	-2.782814000	-0.452544000	4.261662000
H	-2.637741000	-1.449124000	3.791756000
H	-3.391235000	-0.593405000	5.177975000
H	-3.373267000	0.141401000	3.532033000
C	-2.782814000	-0.452544000	-4.261662000
H	-3.391235000	-0.593405000	-5.177975000
H	-2.637741000	-1.449124000	-3.791756000
H	-3.373267000	0.141401000	-3.532033000

2.3. AIM analysis of the computed electron density.

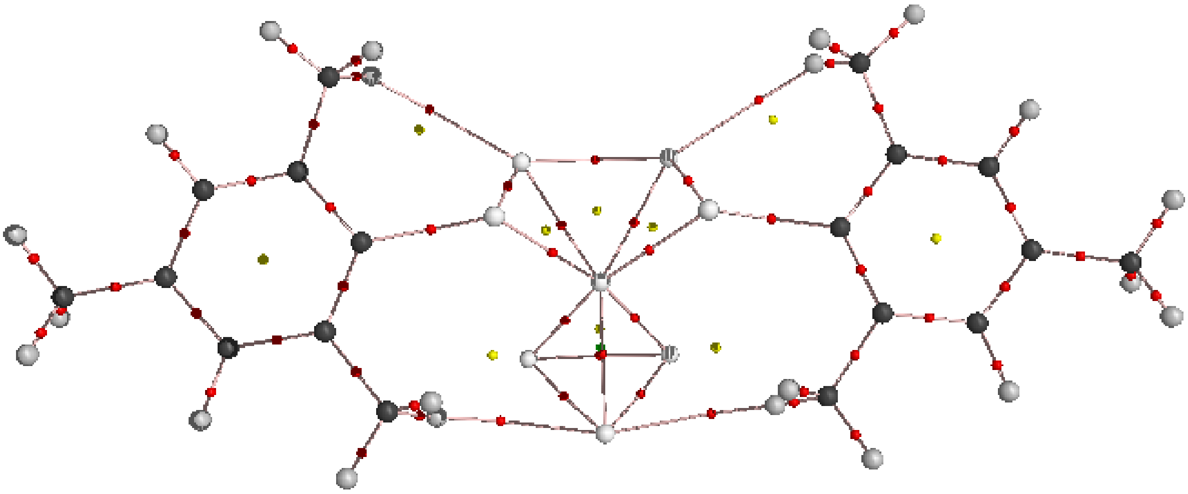

Figure S1: Molecular graph for $\mathbf{1}_{\mathbf{DFT}}$.

Table S2: Selected electron densities ρ(**r**) (e au^{-3}) at the BCPs in $\mathbf{1}_{\mathbf{DFT}}$.

As1–As2	0.085
As2–As3	0.082
As5–As6	0.079
As6–As7	0.081
Co–As1	0.057
Co–As2	0.066
Co–As5	0.069
Co–As6	0.064

3. NMR spectra

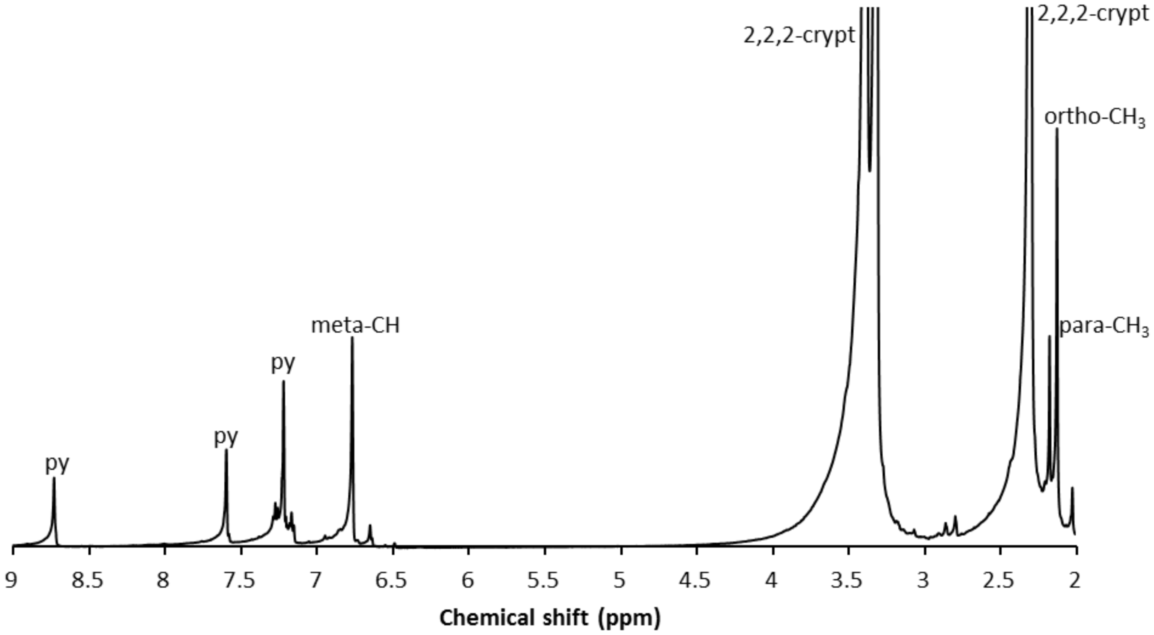

Figure S2. ^{1}H NMR spectrum of a d^5-pyridine solution of [K(2,2,2-crypt)]$_2$[**1**]•py•0.5tol.

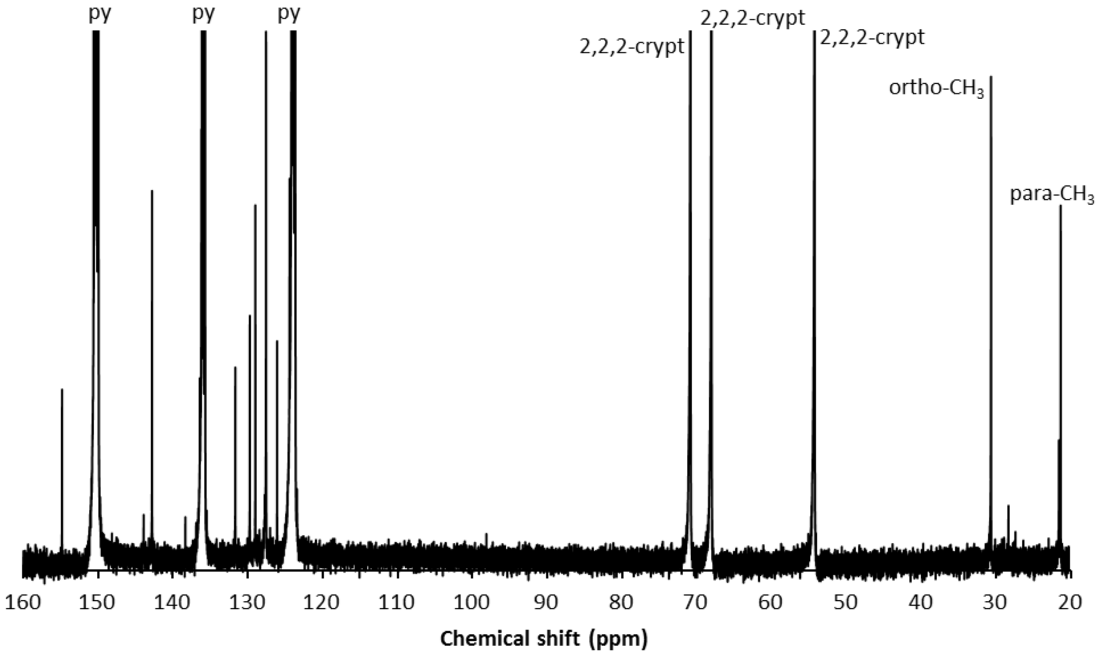

Figure S3. ^{13}C{^{1}H} NMR spectrum of a d^5-pyridine solution of [K(2,2,2-crypt)]$_2$[**1**]•py•0.5tol.

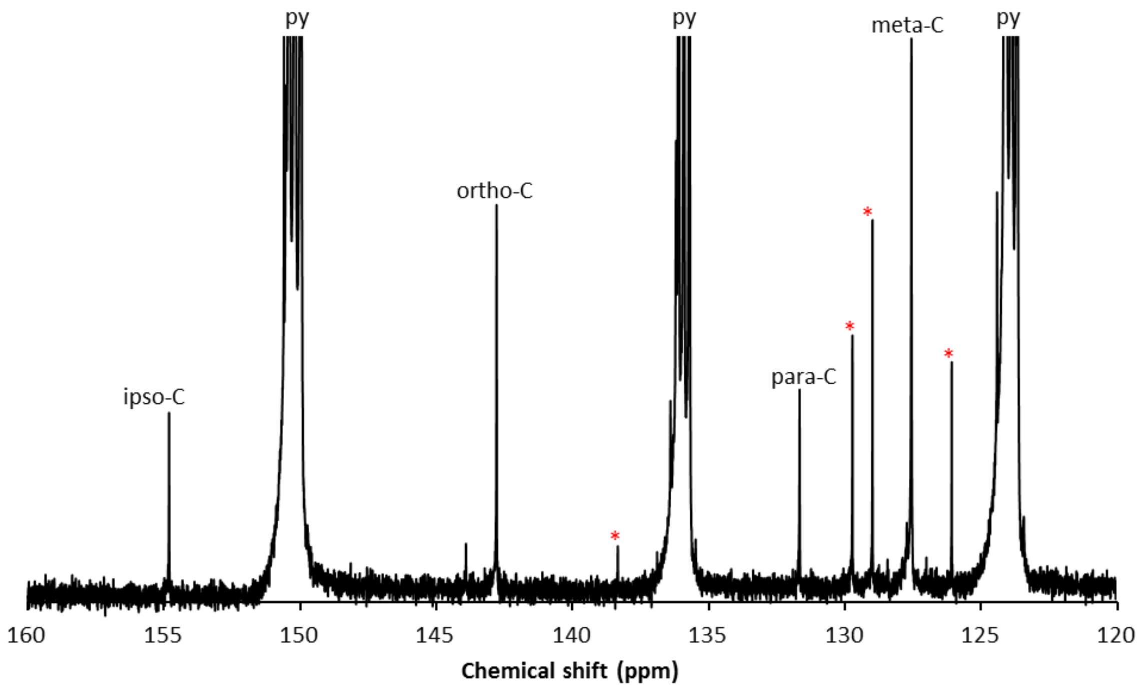

Figure S4. Close-up of the aromatic region of the $^{13}C\{^{1}H\}$ NMR spectrum of $[K(2,2,2\text{-crypt})]_2[\mathbf{1}]$•py•0.5tol. Resonances labelled with a red asterisk correspond to toluene.

4. ESI-MS spectra

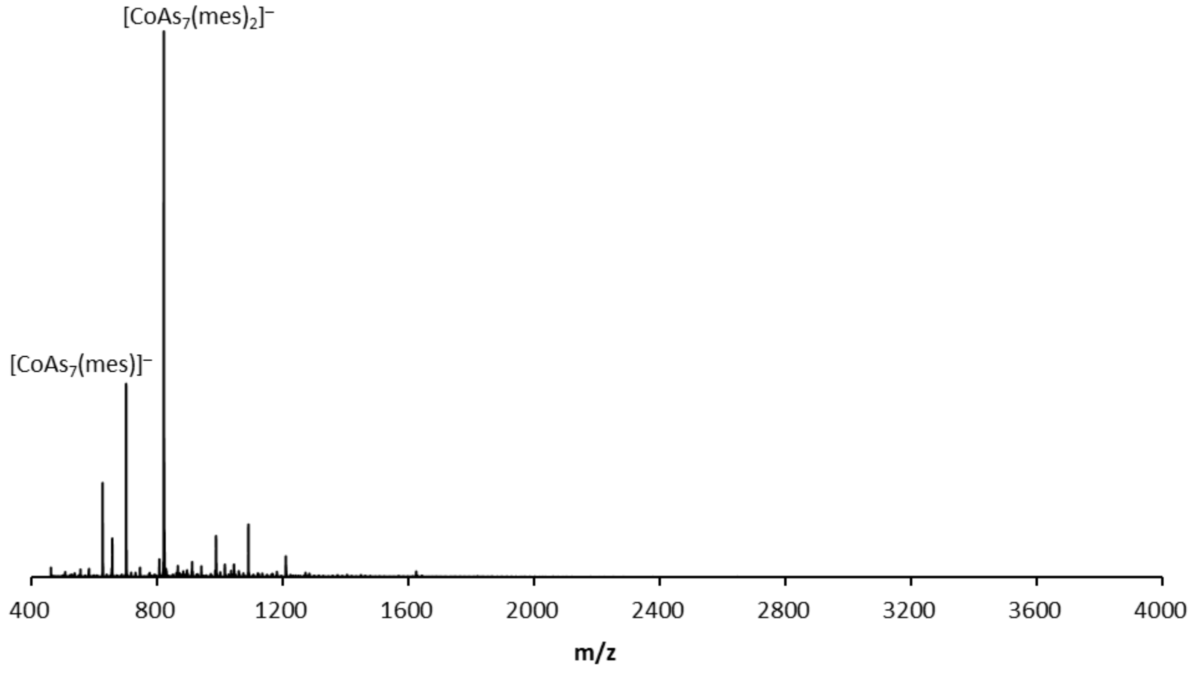

Figure S5. Negative ion mode ESI mass spectrum of a DMF solution of $[K(2,2,2\text{-crypt})]_2[\mathbf{1}]$•py•0.5tol.

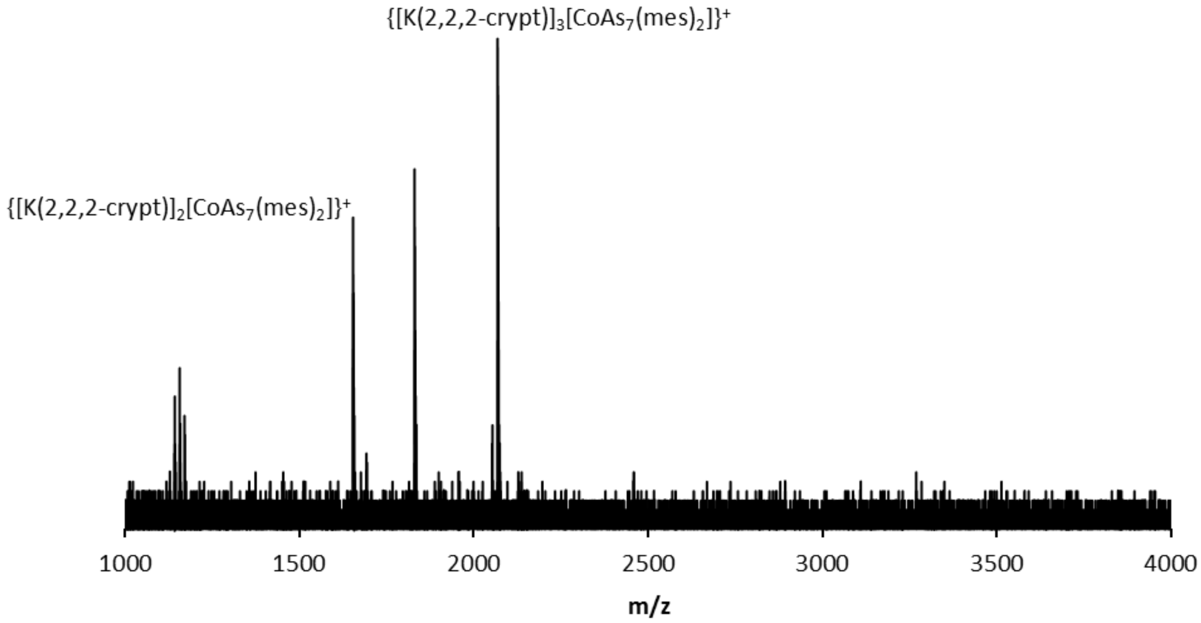

Figure S6. Positive ion mode ESI mass spectrum of a DMF solution of [K(2,2,2-crypt)]$_2$[**1**]•py•0.5tol.

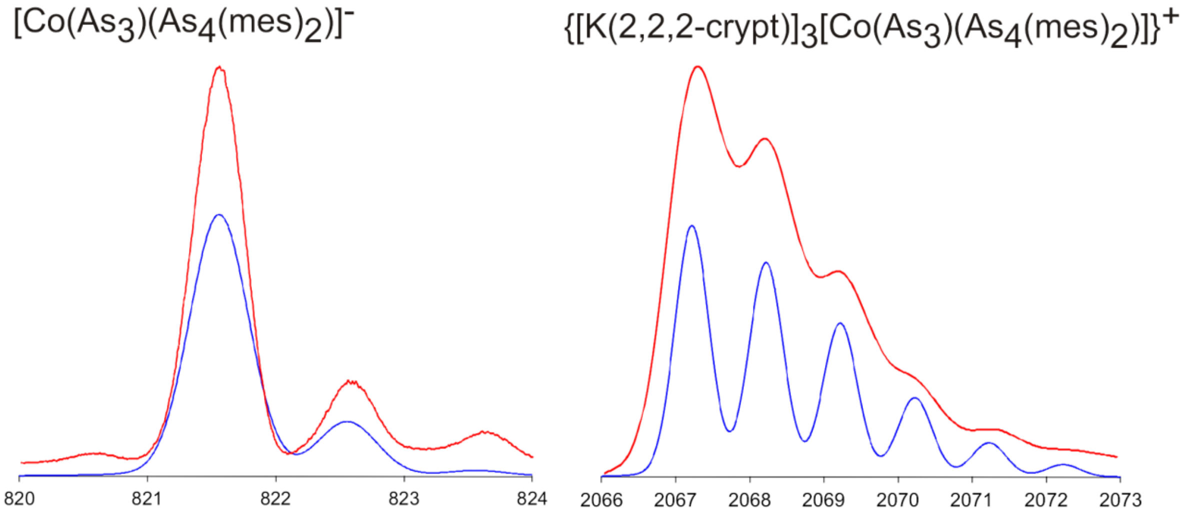

Figure S7. Selected mass envelopes from the negative (left) and positive (right) ESI mass spectra of [K(2,2,2-crypt)]$_2$[**1**]•py•0.5tol. Calculated isotopic distribution patterns are shown in blue while the experimental data are shown in red.

5. References

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