Redox Mediated Dimerisation of a *cyclo*-As_8 Complex

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Supporting Information

Author Contributions

Christoph Riesinger – performing experimental work, acquisition and interpretation of crystallographic data, performance and interpretation of DFT calculations, writing of original draft.

Manfred Scheer – project administration, funding acquisition

All authors contributed in preparing the final manuscript.

Contents

1. Synthesis and Analytical Data

General Considerations

All manipulations were carried out using standard Schlenk techniques at a Stock apparatus under N_2 as an inert gas or in a glove box with Ar atmosphere. All glassware was dried with a heat gun (600 °C) for at least 30 min prior to use. *o*-DFB (1,2-difluorobenzene) was distilled from P_2O_5, CD_2Cl_2 was distilled from CaH_2, THF-d_8 was distilled from Na/K alloy and other solvents were directly taken from an MBraun SPS-800 solvent purification system and degassed at room temperature. Solution ^1H (400.130 MHz) and ^{19}F (376.498 MHz) NMR spectra were recorded at an Avance400 (Bruker) spectrometer using $(H_3C)_4Si$ (^1H), $CFCl_3$ (^{19}F) or 85% phosphoric acid (^{31}P), respectively, as external standards. Chemical shifts (δ) are provided in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). ESI mass spectra were recorded at the internal mass spectrometry department using a ThermoQuest Finnigan TSQ 7000 mass spectrometer and peak assignment was performed using the Molecular weight calculator 6.50.[1] Elemental analysis of the products was conducted by the elemental analysis department at the University of Regensburg using an Elementar Vario EL. The starting materials [{Cp''Ta}$_2$(μ;$\eta^{2:2:2:2:1:1}$-As_8)],[2] [Thia][TEF],[3] [Thia][FAl][3] and KC_8[4] were synthesized following literature procedures. All other chemicals were purchased from commercial vendors and used without further purification.

$[K@crypt]_2[\{Cp''Ta\}_4(\mu_4,\eta^{2:2:2:2:2:2:2:2:1:1:1:1}\text{-}As_{16})]$ (**1**)

$[\{Cp''Ta\}_2(\mu,\eta^{2:2:2:2:1:1}\text{-}As_8)]$ (30 mg, 0.022 mmol, 1 eq.), KC_8 (10 mg, 0.08 mmol, 4 eq.) and [2.2.2]-cryptand (10 mg, 0.027 mmol, 1.2 eq.) were weighed into a Schlenk flask, equipped with a stir bar, and THF (4 mL) was condensed upon the solids. The Schlenk flask was allowed to reach –80 °C and the solution was stirred for 1 h, leading to a color change from light brown to dark brownish black. Afterwards the solution was allowed to reach room temperature and was stirred for another 2 h, the volume of the solvent was reduced to 2 mL and then filtered through glass fiber filter paper. The solution was then layered with 20 mL of *n*-hexane and stored at room temperature. After one week the product $[K@crypt]_2[\{Cp''Ta\}_4(\mu_4,\eta^{2:2:2:2:2:2:2:2:1:1:1:1}\text{-}As_{16})]$ (**1**) could be obtained as dark greenish brown needle and plate shaped crystals.

Yield:	33 mg (0.01 mmol, 90%)
Elemental analysis:	Calculated (%) for $C_{88}H_{156}N_4O_{12}K_2As_{16}Ta_4\cdot(C_4H_8O)_2$: C: 31.97, H: 4.81, N: 1.55; found: C: 31.74 H: 5.32 N: 1.49
^{1}H-NMR (THF-d_8, 300 K):	Crystals of **1** are nearly insoluble in common organic solvents preventing its spectroscopic characterisation.
ESI(+)-MS (DME):	m/z (%) = 415.2 (100, $[K@crypt]^+$)
ESI(-)-MS (DME):	no signals detectable between m/z = 100 – 1600

$[\{Cp''Ta\}_4(\mu_4,\eta^{2:2:2:2:2:2:2:2:1:1:1:1}\text{-}As_{16})][TEF]_2$ (**2**)

$[\{Cp''Ta\}_2(\mu,\eta^{2:2:2:2:1:1}\text{-}As_8)]$ (132 mg, 0.1 mmol, 1 eq.) was dissolved in 4 mL of *o*-DFB and [Thia][TEF] (118 mg, 0.1 mmol, 1 eq.) dissolved in 4 mL of *o*-DFB was added at –30 °C affording a color change to dark brown. The solution was allowed to reach room temperature and was stirred for 6 h. Addition of 40 mL of *n*-pentane lead to the precipitation of a dark, nearly black, solid. The supernatant was decanted, the solid was washed two times with 20 mL of *n*-pentane, each, and the dark solid was dissolved in 3 mL of *o*-DFB. After filtration, the product $[\{Cp''Ta\}_4(\mu_4,\eta^{2:2:2:2:2:2:2:2:1:1:1:1}\text{-}As_{16})][TEF]_2$ (**2**) was precipitated by the addition of 60 mL of *n*-hexane and could be isolated as dark brown powder. Recrystallisation by layering a concentrated solution of **2** in 2 mL of *o*-DFB with 40 mL of *n*-pentane and storage at 4 °C afforded dark brown rod-shaped crystals of the title compound after two weeks.

Yield:	182 mg (0.04 mmol, 80%)
Elemental analysis:	Calculated (%) for: $C_{84}H_{84}O_8F_{72}Al_2As_{16}Ta_4$: C: 22.10, H: 1.85; found: C: 22.58 H: 2.19
^{1}H-NMR (CD_2Cl_2, 300 K):	δ/ ppm = 1.28 (s (br), 36 H, $C_5H_3{}^tBu_2$), 1.35 (s (br), 36 H, $C_5H_3{}^tBu_2$), 4.62 (s (br, 2 H, $C_5H_3{}^tBu_2$), 4.90 – 5.62 (very broad overlapping signals, 10 H, $C_5H_3{}^tBu_2$)
$^{19}F\{^1H\}$-NMR (CD_2Cl_2, 300 K):	–75.6 (s, $[TEF]^-$)
ESI(+)-MS (*o*-DFB):	m/z (%) = 1315.6 (100, $[\mathbf{2}]^{2+}$)

Formation of $[\{Cp''Ta\}_2(\mu,\eta^{3:3}\text{-}As_6)][TEF]$ (**3**) and $[\{Cp''Ta\}_6(\mu_6,\eta^{2:2:2:2:2:2:2:2:2:2:2:2:1:1:1:1:1:1}\text{-}As_{25})][TEF]_3$ (**4**)

Prolonged periods (1 – 2 weeks) of crystallisation of **2** are accompanied by partial disproportionation to the arsenic depleted $[\{Cp''Ta\}_2(\mu,\eta^{3:3}\text{-}As_6)][TEF]$ (**3**) and the formation of an arsenic rich side product. While **3** cocrystallises with **2**, additional black and block-shaped crystals of $[\{Cp''Ta\}_6(\mu_6,\eta^{2:2:2:2:2:2:2:2:2:2:2:2:1:1:1:1:1:1}\text{-}As_{25})][TEF]_3$ (**4**) can be observed besides the rod-shaped **2** (and **3**). While crystals of **4** themselves have too low quality for obtaining reliable crystallographic data, it could be crystallised as the mixed $[FAl]^-/[SbF_6]^-$ ($[FAl]^-$ = $[FAl\{O(1\text{-}C_6F_5)C_6F_{10}\}_3]^-$) salt after using a mixture of [Thia][FAl] and $Li[SbF_6]$ as oxidizing agent. Nevertheless, both disproportionation compounds **3** and **4** are inseparable (**3** even co-crystallises with **2**) and could thus not be characterised spectroscopically or isolated in quantifiable yields. However, mass spectrometric measurements of the product mixture confirmed the presence of both **3** and **4** and corroborated their structural integrity. Lastly, attempts to supress or modulate the disproportionation of 2 in solution via either choice of solvent (CH_2Cl_2, *o*-DFB), change in temperature (-30 °C to 25 °C), or the exchange of the counter anion were all unsuccessful.

ESI(+)-MS (*o*-DFB):	m/z (%) = 193.2 (100, $[Cp''O]^+$), 807.6 (60, unidentified), 1061.6 (35, unidentified) 1165.8 (20, $[\mathbf{3}]^+$), 1315.6 (50, $[\mathbf{2}]^{2+}$), 1340.6 (50, $[\mathbf{4}]^{3+}$)

2. Cyclovoltammetry of [{Cp''Ta}$_2$(μ,η$^{2:2:2:2:1:1}$-As$_8$)]

To get an initial idea of the redox behavior of [{Cp''Ta}$_2$(μ,η$^{2:2:2:2:1:1}$-As$_8$)] (**A**), cyclovoltammetric (CV) measurements were performed. **A** (30 mg) was dissolved in 10 mL of *o*-DFB, 1 g of [^{n}Bu$_4$N][PF$_6$] were added and the measurements were performed on these solutions. The CV of **A** in between +1.4 V and –1.5 V (vs. Fc/Fc$^+$, Figure S 1) overall reveals four irreversible redox processes. Two of these are oxidative and two are reductive redox events. However, only the redox events at -1441 mV (vs. Fc/Fc$^+$, reduction) and 294 mV (vs. Fc/Fc$^+$, oxidation) were considered for synthetic application within this study. The redox events at -2335 mV and 969 mV are close to the borders of the solvent window (*o*-DFB) and were not studied synthetically in further detail. Attempts to increase the electrochemical reversibility in this system by decreasing the concentration of the analyte **A** were unsuccessful as they did not produce cyclic voltammograms of high enough quality.

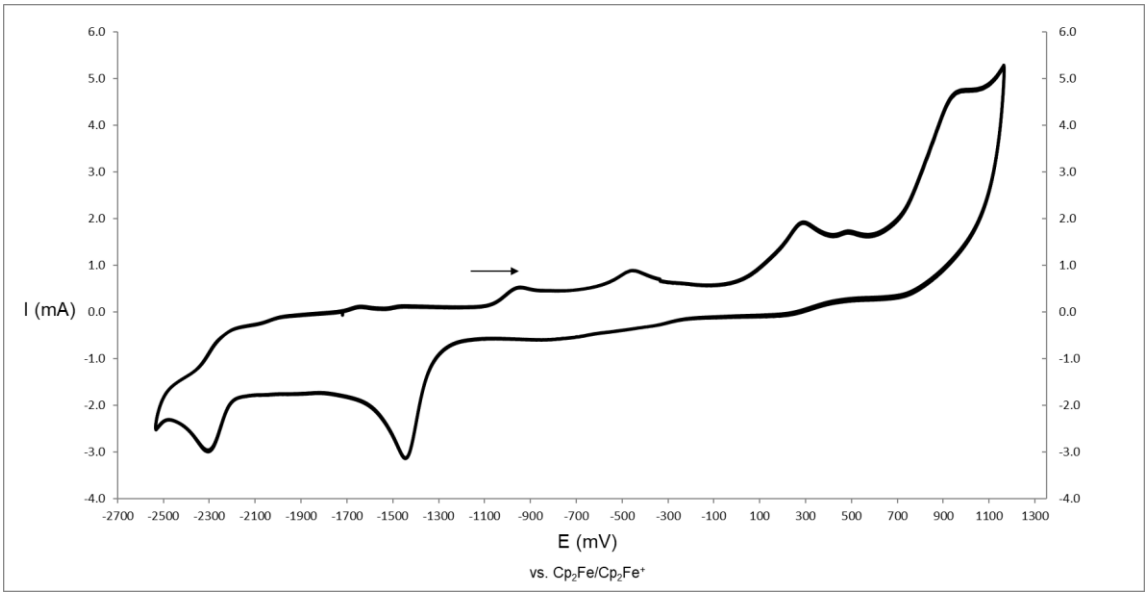


*Figure S 1 Cyclovoltammogram of **A** from -2.7 V to 1.3 V (30 mg in 10 mL o-DFB with 1000 mg [^{n}Bu$_4$N][PF$_6$] as supporting electrolyte).*

3. X-ray Crystallographic Data

General Considerations

The crystallographic data for all synthesised compounds was collected on an XtaLAB Synergy R, DW System (Rigaku) with a HyPix-Arc 150 detector using Cu-Kα radiation from a rotating anode (**1**, **2**, **3**), or on a GV50 diffractometer (Rigaku) with a Titan^{S2} detector using a standard Cu–Kα (**4**) sealed tube microfocus source. Data reduction and absorption correction were performed with the CrysAlisPro software package.[5] Structure solution and refinement was conducted in Olex2 (1.5-alpha)[6] with ShelXT[7] (solution) and ShelXL-2014[8,9] (least squares refinement (F^2)). All non-H atoms were refined with anisotropic displacement parameters and H atoms were treated as riding models with isotropic displacement parameters and fixed C–H bond lengths (sp^3: 0.96 (CH3), 0.97 (CH2); sp^2: 0.93 (CH)). Visualisation of the crystal structures was performed with Olex2 (1.5-alpha).[6]

CIF files with comprehensive information on the details of the diffraction experiments and full tables of bond lengths and angles for **1** – **4** are deposited in Cambridge Crystallographic Data Centre under the deposition codes CCDC-2421973 (**1**), CCDC-2421974 (**2-3**), and CCDC-2421976 (**4**), respectively.

*Table S 1: X-ray crystallographic data on compounds **1** – **4**.*

Compound	**1**	**2/3**	**4**
Empirical formula	$C_{56}H_{102}As_8KN_2O_9Ta_2$	$C_{50.5}H_{52}AlAs_{7.09}F_{38}O_4Ta_2$	$C_{177}H_{180}Al_2As_{25}F_{99}O_6SbTa_6$
Formula weight	1929.72	2364.83	3709.30
Temperature/K	123.00(10)	123.00(10)	123.00(10)
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	C2/c
a/Å	15.0885(3)	11.4386(2)	24.4761(3)
b/Å	15.7216(3)	18.7072(4)	36.8173(5)
c/Å	17.5225(4)	19.1356(5)	28.1239(3)
α/°	109.352(2)	63.108(2)	90
β/°	108.366(2)	88.564(2)	100.6410(10)
γ/°	101.935(2)	76.688(2)	90
Volume/Å3	3489.97(14)	3539.01(15)	24907.9(5)
Z	2	2	4
ρcalcg/cm3	1.836	2.219	1.978
μ/mm-1	10.816	6.532	10.396
F(000)	1886.0	2244.0	14084.0
Crystal size/mm3	0.35 × 0.14 × 0.06	0.07 × 0.06 × 0.03	0.319 × 0.121 × 0.042
Radiation	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.878 to 151.99	4.136 to 61.016	7.176 to 147.692
Index ranges	-15 ≤ h ≤ 18, -19 ≤ k ≤ 17, -21 ≤ l ≤ 21	-16 ≤ h ≤ 14, -26 ≤ k ≤ 26, -27 ≤ l ≤ 27	-29 ≤ h ≤ 30, -42 ≤ k ≤ 44, -31 ≤ l ≤ 34
Reflections collected	45895	116687	47169
Independent reflections	13518 [R_{int} = 0.0804, R_{sigma} = 0.0609]	21595 [R_{int} = 0.0919, R_{sigma} = 0.0674]	24241 [R_{int} = 0.0399, R_{sigma} = 0.0467]
Data/restraints/parameters	13518/0/625	21595/2123/1547	24241/145/1408
Goodness-of-fit on F2	1.166	1.015	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0591, wR_2 = 0.1755	R_1 = 0.0651, wR_2 = 0.1529	R_1 = 0.0559, wR_2 = 0.1495
Final R indexes [all data]	R_1 = 0.0708, wR_2 = 0.1914	R_1 = 0.1135, wR_2 = 0.1735	R_1 = 0.0604, wR_2 = 0.1544
Largest diff. peak/hole / e Å-3	2.41/-2.80	1.57/-0.80	2.51/-2.29

$[K@crypt]_2[\{Cp''Ta\}_4(\mu_4;\eta^{2:2:2:2:2:2:2:2:1:1:1:1}\text{-}As_{16})]$ (**1**)

Layering a concentrated solution of **1** in THF with *n*-hexane leads to formation of dark greenish brown needle-shaped and plate-shaped crystals after seven days of storage at room temperature. **1** crystallizes in the triclinic space group $P\bar{1}$ with half of the dianion, one cation and three molecules of THF in the asymmetric unit, which is depicted in Figure S 2. A solvent mask has been used for two of the disordered THF molecules.

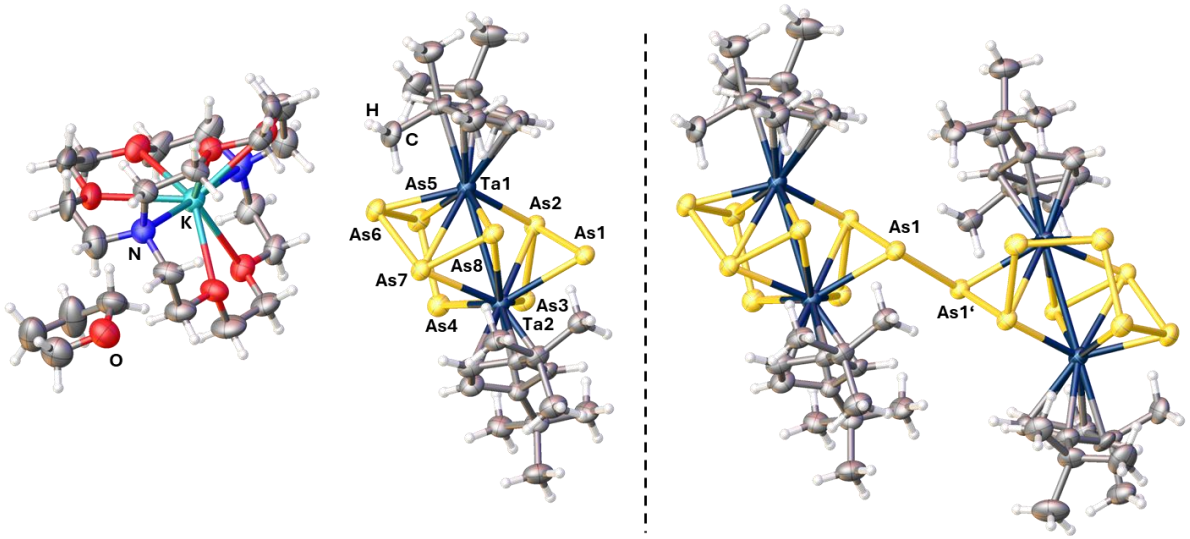


*Figure S 2: Asymmetric unit of compound **1** in the solid state (left) and the molecular structure of the dianionic core of **1** (right); anisotropic displacement parameters are drawn at the 50% probability level; Selected bond lengths: As1-As2 (2.404(1) Å), As2-As3 (2.403(1) Å), As3-As4 (2.404(1) Å), As4-As5 (2.437(1) Å), As5-As6 (2.385(1) Å), As6-As7 (2.458(1) Å), As7-As8 (2.415(1) Å), As1-As8 (3.083(1) Å), As1-As1' (2.441(1) Å), Ta1-Ta2 (3.354(1) Å);*

$[\{Cp''Ta\}_4(\mu_4,\eta^{2:2:2:2:2:2:2:2:1:1:1:1}\text{-}As_{16})][TEF]_2$ (**2**) and $[\{Cp''Ta\}_2(\mu,\eta^{3:3}\text{-}As_6)][TEF]$ (**3**)

Layering a concentrated solution of **2** in *o*-DFB with *n*-pentane leads to formation of dark rod-shaped crystals after two weeks of storage at 4 °C. **2** crystallizes in the triclinic space group $P\bar{1}$ with half of the dication, one anion, one molecule of *o*-DFB and half of a molecule of *n*-pentane in the asymmetric unit, which is depicted in Figure S 3. A solvent mask has been used for the *o*-DFB and the *n*-pentane molecules and disorder has been treated with adequate restraints. In addition, compound **3** cocrystallises with nearly equivalent Ta positions compared to **2**, which has been modelled as disorder. The ratio in occupancy of **2**:**3** is 0.54:0.46. Due to this complex disorder the bond lengths for both **2** and **3** should be considered carefully. Especially the As1-As1' distance for compound **2** is underestimated. This issue is intensified due to the symmetry within compound **2**.

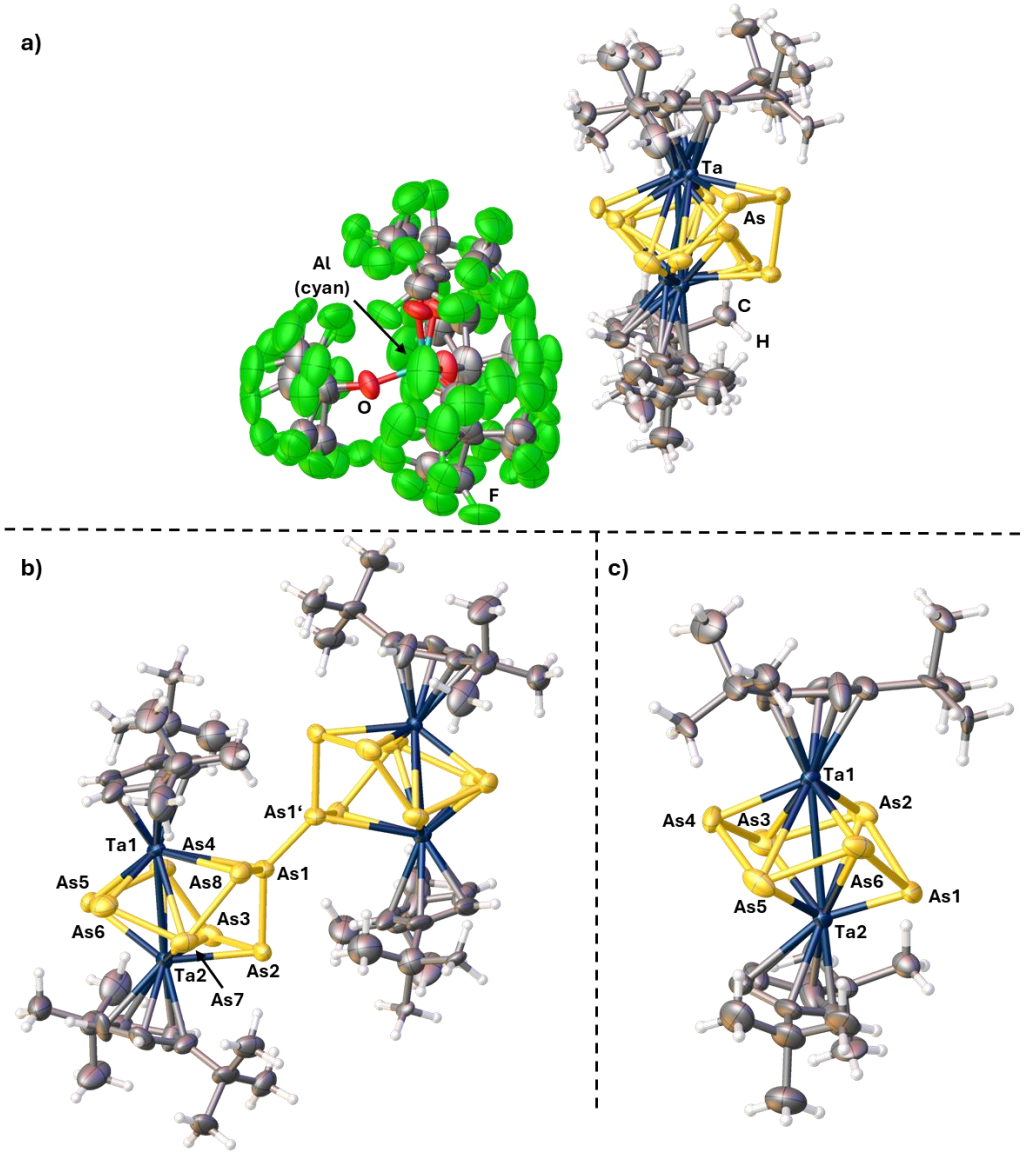


*Figure S 3: Asymmetric unit of compound **2** in the solid state (a), the molecular structure of the dicationc core of **2** (b) and the isolated molecular structure of the triple-decker cation in **3** (c); anisotropic displacement parameters are drawn at the 50% probability level; Selected bond lengths for **2**: As1-As2 (2.423(3) Å), As2-As3 (2.370(2) Å), As3-As4 (2.422(3) Å), As4-As5 (2.421(2) Å), As5-As6 (2.621(2) Å), As6-As7 (2.411(1) Å), As7-As8 (2.493(2) Å), As1-As8 (2.392(3) Å), As1-As1' (2.120(3) Å, this bond length is significantly underestimated by the experimental data due to the complex disorder within the cationic part of this crystal structure), Ta1-Ta2 (3.253(3) Å); Selected bond lengths for **3**: As1-As2 (2.486(3) Å), As2-As3 (2.507(4) Å), As3-As4 (2.380(3) Å), As4-As5 (2.411(1) Å), As5-As6 (2.728(2)), As1-As6 (2.545(3) Å), Ta1-Ta2 (3.342(3) Å).*

[{Cp''Ta}$_6$(μ_6,$\eta^{2:2:2:2:2:2:2:2:2:2:2:1:1:1:1:1:1:1}$-$As_{25}$)][FAl]$_2$[$SbF_6$] (**4**)

Compound **4** crystallises besides the cocrystals of **2** and **3** after prolonged (1 – 2 weeks in solution) times of storage and forms nearly black block-shaped crystals. While the crystal quality of [{Cp''Ta}$_6$(μ_6;$\eta^{2:2:2:2:2:2:2:2:2:2:2:1:1:1:1:1:1:1}$-$As_{25}$)][TEF]$_3$ was too low to obtain reliable crystallographic data, its mixed [FAl]$^-$/[SbF_6]$^-$ salt could be obtained using a related oxidation agent (*vide supra*) and under similar crystallisation conditions (replacing *n*-pentane with *n*-hexane). Nevertheless, compound **4** is inseparable from the other ionic species in this mixture. The mixed [FAl]$^-$/[SbF_6]$^-$ salt of **4** crystallises in the monoclinic space group *C*2/*c* with half of the trication, one [FAl]$^-$ anion, half of an [SbF_6]$^-$ anion, one molecule of *o*-DFB and two molecules of *n*-hexane in the asymmetric unit, which is shown in Figure S 4. A solvent mask has been used for the *n*-hexane molecules and disorder has been treated with adequate restraints

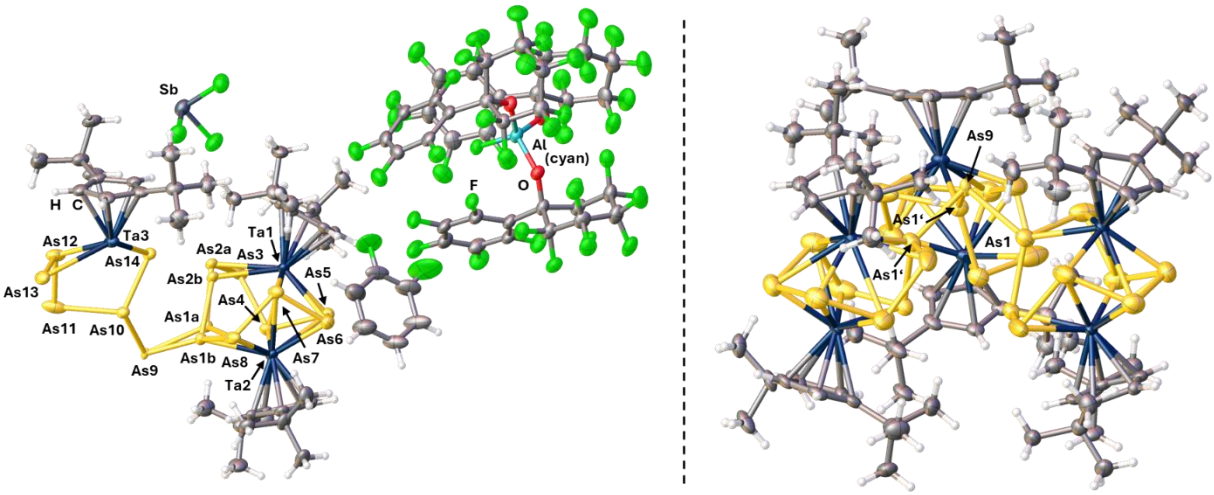


*Figure S 4: Asymmetric unit of compound **4** in the solid state (left) and the molecular structure of the tricationic core of **3** (right); anisotropic displacement parameters are drawn at the 50% probability level; Selected bond lengths and distances: As1a-As2a (2.426(2) Å), As1b-As2b (2.435(2) Å), As2a-As3 (2.164(2) Å), As2b-As3 (2.591(2) Å), As3-As4 (2.417(1) Å), As4-As5 (2.406(1) Å), As5-As6 (2.537(1) Å), As6-As7 (2.402(1) Å), As7-As8 (2.419(1) Å), As8-As1a (2.571(2) Å), As8-As1b (2.196(2) Å), As1a-As9 (2.533(2) Å), As1b-As9' (2.549(2) Å), As9-As10 (2.553(2) Å), As10-As11 (2.611(2) Å), As10-As14 (2.426(2) Å), As11-As12 (2.421(1) Å), As12-As13 (2.403(1) Å), Ta1-Ta2 (3.352(1) Å), Ta3-Ta3' (3.376(1) Å).*

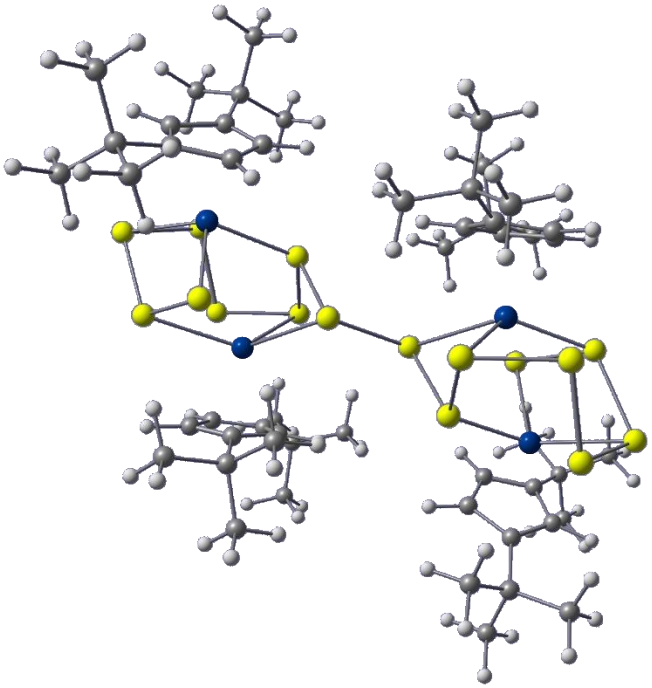
4. Computational Data

General Remarks

DFT calculations were performed using the Orca 5.0.4 software package.[10–14]. Geometry optimizations were performed at the BP86[15]/def2-SVP[16] level of theory with PCM solvent correction[17] for THF (**1**) and CH_2Cl_2 (**2**), respectively. Stationary points were verified by analytical frequency calculations. Single point calculations and NBO analysis (NBO 7.0)[18] were performed at the ωB97X-D4[19–22]/def2-TZVP level of theory with solvent correction as described above. Images of calculated structures were generated with ChemCraft.[23]

Optimised Geometries

1



Ta	5.50703480007848	5.02551615771751	2.18996553835960
Ta	8.71734845869267	3.86980771323389	1.66366294264327
As	7.94292655370333	6.36946253101256	1.70809473743638
As	6.47994592526418	7.18040812910426	3.51122524217045
As	6.27383938124667	6.47952164927724	-0.08076198443007
As	6.67261732897188	3.28935727583177	0.23333118671380
As	6.31889228014803	2.48976836089625	2.53084288868153
As	6.50981858542340	5.11579839629673	4.78373139605499
As	8.53555973960537	2.17221237677389	3.66131314788586
As	8.86411320250272	4.46674591644114	4.36876038789074
C	3.05725432296891	2.35485671077837	-0.27873347751463
H	4.14091949449510	2.12443428780099	-0.22738023480317
H	2.67127567409151	1.98052153119585	-1.24991867613097
H	2.54150612860797	1.78841952396660	0.52390398209879
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H	3.27915565146515	5.69428937854101	-1.31609167619964
H	2.95662942587585	4.24179902738656	-2.31384256138074
H	4.51680167352407	4.40450186027678	-1.43262733658133
C	3.29333379773423	5.94326234096236	2.99445579370088
C	3.25495846513355	5.82207568108447	1.56211199065599
H	3.10088052995522	6.65752098824892	0.86728964253847

C	11.17983449619216	4.23673171764716	1.39351007795286
C	3.27891228389085	7.12475416114720	5.26563783713913
H	4.37897649926849	7.26440632721033	5.30003384480929
H	3.04370656204888	6.17973384563711	5.79651480410226
H	2.81064280556565	7.95369973511262	5.83634870812935
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C	3.02879187603405	8.48835301574318	3.16327262685390
H	2.63536917901353	8.53782792270056	2.12804823408277
H	4.11560028830084	8.70019052236442	3.11731340539367
H	2.54054047367050	9.29547485310196	3.74842474280669
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H	3.47986684872739	2.59956601420929	2.49060709213012
C	3.49299900908857	4.61211141852647	3.49989723749949
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C	9.10199699625798	1.21743944617093	-1.77994765803288
H	9.54782622297365	1.86347062153562	-2.56409878166398
H	8.09436897151923	1.61499047539886	-1.53659693190014
H	8.97871128670316	0.20237951213706	-2.21143805229267
C	11.40199046809126	0.65044072859171	-0.93991620362717
H	11.32769244060443	-0.34037023300956	-1.43632628510588
H	12.06908654924007	0.54393572764936	-0.06035173595802
H	11.88097831558144	1.35573864004614	-1.65036595769602
C	1.26370992847958	4.10649764706315	-0.18830556983107
H	0.76795572069437	3.61237765150112	0.67317976174448
H	0.82736285079172	3.68976157763178	-1.12095042194118
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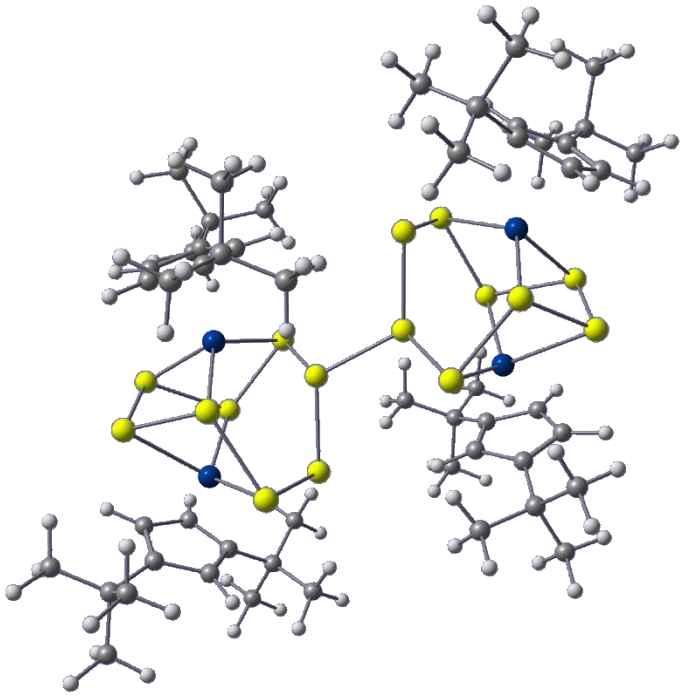
2



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