Trapping CS₂²⁻ and S₃²⁻ Between Two Ytterbium Formamidinates.

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Disorder of [Yb₂(DippForm)₄(CS₂)]:



Figure S1. Structure of $[Yb_2(DippForm)_4(CS_2)] \cdot (0.5PhMe)$ showing disorder of the CS₂ group. Ellipsoids shown at 20% probability, hydrogen atoms and lattice solvent were removed, and the methyl groups of the isopropyl groups have been simplified as "iPr" for clarity. Furthermore, there were two identified Yb centres (Yb1A: 90% occupancy, Yb2A: 10% occupancy), the bond lengths presented are for Yb1A: *Disorder*: the CS₂ fragment is disordered over a special position (namely on the *a*, *b*, *c* axes), which generates four CS₂ arrangements (see below). Selected bond lengths (Å): Yb1A-N1: 2.305(4), Yb1A-N2: 2.342(6), Yb1A-N3: 2.309(5), Yb1A-N4: 2.373(6), selected bond angles (°): S2A-C1B-S1A: 143.0(4), S1B-C1A-S2B: 140.3(5).

Disorder arrangements one and two:



Disorder arrangements three and four:



Distances between symmetry equivalent atoms



Note: Refinement without **S1A/S1B** leads to unstable refinement for C atoms (**C1A/C1B**). Bond angle (°): S2B-C1A-S2B': 79.4(8), S2A-C1B-S2A': 79.3(8).





Figure S2. Structure of $[Yb_2(DippForm)_4(S_2)_{0.5}/(S_3)_{0.5}] \cdot (0.5PhMe)$. Ellipsoids shown at 20% probability, hydrogen atoms were removed, and the methyl groups of the isopropyl groups have been simplified as "iPr" for clarity. See below for part breakdown. Selected bond lengths (Å): Yb1-N1: 2.531(10), Yb1-N2: 2.300(8), Yb1-N3: 2.297(7), Yb1-N4: 2.339(7), Yb1-S1: 2.587(5), Yb1-S2: 2.735(6), Yb1-S3 (non-bond): 3.756(8), Yb1-S1A: 2.860(6), Yb1-S2A: 3.078(10), Yb2-N5: 2.344(8), Yb2-N6: 2.293(8), Yb2-N7: 2.312(7), Yb2-N8: 2.336(8), Yb2-S1A: 2.887(6), Yb2-S2A: 2.793(8), Yb2-S3: 2.527(11), Yb2-S2: 2.818(6), Yb2-S1 (non-bond): 3.881(5), S1-S2: 2.118(9), S1A-S2A: 2.174 (8), S3-S2: 2.153(9). Selected bond angles (°): Yb1-S2-Yb2: 151.4(2), Yb1-S1A-Yb2: 139.4(4), Yb1-S2A-Yb2: 132.8(2), S1-S2-S3: 109.0(4).

Disorder arrangements one and two for $[Yb_2(DippForm)_4(S_2)_{0.5}/(S_3)_{0.5})](0.5PhMe)$:



Structure of [Yb₂(DippForm)₄(S₂)](2DippFormH)₂(2.5C₆D₆)



Figure S3.1. Crystal structure of $[Yb_2(DippForm)_4(S_2)](2DippFormH)_2(2.5C_6D_6)$ ellipsoids shown at 30% probability. Hydrogen atoms (except H1L and H4L) and lattice solvent were removed for clarity.



Figure S3.2. [Yb₂(DippForm)₄(S₂)] fragment of

 $[Yb_2(DippForm)_4(S_2)](2DippFormH)_2(2.5C_6D_6)$, ellipsoids shown at 30% probability, and hydrogen atoms plus lattice solvent were removed for clarity. Selected bond lengths (Å): Yb1-N1: 2.335(8), Yb1-N2: 2.326 (7), Yb1-N3: 2.333(7), Yb1-N4: 2.330(8), Yb1-S1: 2.721(3), Yb1-S1': 2.721(3), S1-S1': 2.127(7), Yb1-S1-Yb1': 133.73(13).



Figure S3.3. View of [Yb₂(DippForm)₄(S₂)] fragment down the Yb-Yb axis.

Table S1.1 Table of crystallographic data:

Complex	[Yb ₂ (DippForm) ₄ (CS ₂)].(0.5PhMe)	[Yb ₂ (DippForm) ₄ (S ₂) _{0.5} (S ₃) _{0.5}](0.5PhMe)	[Yb ₂ (DippForm) ₄ (S ₂)](2DippFormH) ₂ (2.5C ₆ D ₆)
Empirical formula	$C_{105.5}H_{145}N_8S_2Yb_2$	$C_{100}H_{140}N_8S_{2.5}Yb_2$	$C_{215}H_{299}N_{16}S_2Yb_2$
Code	3	4	5
Formula weight	1935.49	1926.49	3517.88
CCDC number	1869038	1869040	1869039
Temperature/K	100	100	100
Crystal system	monoclinic	triclinic	monoclinic
Space group	C2/c	<i>P</i> -1	<i>C</i> 2/ <i>c</i>
a/Å	26.955(5)	14.612(3)	32.827(7)
b/Å	14.702(3)	15.210(3)	28.336(6)
c/Å	29.554(6)	27.542(6)	22.088(4)
α/°	90	85.99(3)	90
β/°	116.39(3)	76.11(3)	91.66(3)
γ/°	90	63.52(3)	90
Volume/Å ³	10491(4)	5314(2)	20537(7)
Z	4	2	4
$\rho_{calc}g/cm^3$	1.225	1.204	1.138
μ/mm ⁻¹	1.858	1.843	0.978
F(000)	4024	2002	7492
Crystal size/mm ³	$0.2 \times 0.1 \times 0.1$	$0.1 \times 0.03 \times 0.02$	$0.1 \times 0.02 \times 0.01$
Radiation	Synchrotron	Synchrotron	Synchrotron
20 range for data collection/°	3.922 to 54.998	1.524 to 55	1.9 to 52.052
Index ranges	-34 ≤ h ≤ 34, -19 ≤ k ≤ 19, -38 ≤ l ≤ 38	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -35 ≤ l ≤ 35	$-40 \le h \le 40$, $-34 \le k \le 34$, $-0 \le l \le 27$
Reflections collected	46969	107680	20169
Independent reflections	11994 [R _{int} = 0.0778, R _{sigma} = 0.0545]	24218 [R_{int} = 0.1108, R_{sigma} = 0.0713]	20169 [R_{int} = merged ^{3a} , R_{sigma} = 0.0535]
Data/restraints/parameters	9226/461 ^{1a} /610	24218/160 ^{2a} /1200	20169/67 ^{3b} /1087
Goodness-of-fit on F ²	1.057	1.050	1.157
Final R indexes [I>=2σ (I)]	$R_1 = 0.0657$, $wR_2 = 0.1787$	$R_1 = 0.0972$, $wR_2 = 0.2461$	$R_1 = 0.0980$, $wR_2 = 0.2549$
Final R indexes [all data]	$R_1 = 0.0816$, $wR_2 = 0.1904$	$R_1 = 0.1222$, $wR_2 = 0.2638$	$R_1 = 0.1093$, $wR_2 = 0.2604$
Largest diff. peak/hole / e Å ⁻³	1.31 ^{1b} /-1.37	4.52 ^{2b} /-3.65	4.93 ^{3c} /-3.94

1. A) ISOR commands used on disordered isopropyl groups of DippForm, XYZ restraint used on C/S atoms of CS₂ ligand, with majority of constraints used on the disorder toluene molecule within the lattice. B) large residual peak next to Yb atom (5.56), could be removed when ytterbium atom was split 90:10 with refined with PART refinement. Bond displayed are used for the 90% occupancy.

2. A) Isopropyl groups were disordered across two positions, refined with PART refinement and ISOR commands were used to constrain Me groups which could not be split. Solvent mask within Olex 2 was used to remove electron density (5 elctrons) from near the Ytterbium centre, two partially disordered quarter toluene molecules were identified within the lattice. B) disordered lattice solvent. large residual peak next to Yb atom (1.0427 Å & 0.9178 Å) due to absorption anomaly. Solvent mask used to remove low occupancy residual peaks (2 x 6.4 e-, and X 5.3 e-)

3. A) TWINNED data refinement, PLATON merged. B) ISOR command used on disordered isopropyl groups and one carbon atom of a phenyl ring that gave NPD. Solvent mask within Olex 2 was used to remove low occupancy disordered lattice solvent (C₆D₆). C) Three large residual peaks next to the Yb atom (1.3805(4) Å, 0.8533(5) & 1.3742(8) Å) due to absorption anomaly and slight crystal twinning – attempted refinement for a second Yb atom in partial refinement was unsuccessful.

X-ray crystallography details: For a table of crystallographic details please refer to the Supporting information. All compounds were examined on either the MX1¹ or MX2² beamlines at the Australian synchrotron. Absorption corrections were completed using SADABS.³ Data integrations were completed using Blueice,⁴ structural solutions were obtained by ShelXT⁵ using full matrix least squares methods against F2 using SHELX2015,⁵ within the OLEX 2 graphical interface.⁶ Refer to supporting information for full structural details. CCDC data for complexes **3** (1869038), **4** (1869040), and **5** (1869039) can be obtained free of charge from the Cambridge Crystallographic Data Centre.

References:

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Figure S4.1. ¹H NMR spectrum (C_6D_6 , 300 K, 300 MHz) of the reaction between CS_2 and excess [Yb(DippForm)₂(thf)], indicating the presence of [Yb(DippForm)₂(thf)] (**B** = N=CH-N, **C** = iPr) and liberated THF (**C**, **D**).



Figure S4.2. ¹H NMR (C₆D₆, 300 K, 300 MHz) spectrum of the reaction between CS₂ and [Yb(DippForm)₂(thf)], with excess CS₂



Figure S4.3. ¹H NMR (C_6D_6 , 300 K, 300 MHz) expanded spectrum of the reaction between CS₂ and [Yb(DippForm)₂(thf)], with excess CS₂





Figure S5. ¹H NMR (C₆D₆, 300 K, 300 MHz) spectrum of the reaction mixture between [Yb(DippForm)₂(thf)] and excess elemental sulfur.



Figure S6. IR spectrum of compound 3.