Supplementary data

Arene-ligated Heteroleptic Terphenolate Complexes of Thorium

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Crystal Structure Determinations

General Details

X-ray crystallographic data for **1a**, **2-4** were collected at 170 K on an Oxford Diffraction Excalibur diffractometer using graphite monochromated Mo-Kα radiation equipped with an Eos CCD detector. Data for **1b** was collected at 120(2) K on a Supernova dual source Atlas diffractometer, utilising the Cu $K\alpha$ source. Structures were solved using either SHEL-XS-13 direct methods,[1] SHEL-XS-13 Patterson methods,[1] or the SUPERFLIP charge-flipping program[2] and refined using a full-matrix least square refinement on $|F|^2$ using SHELXL-13.[1] All programs were used within the WinGx suite.[3] All non-H atoms were refined anisotropically and all H atoms (except for the BH_4 hydrogens) were placed in calculated positions and refined using a riding model.

In **1a**, the C27-C28 bond was fixed to 1.53(2) Å. The SIMU (su 0.04 A_2) and DELU (su 0.01 A_2) commands were applied to the atoms of one of the co-crystallised toluene solvent molecules to normalise the magnitude and direction of the atomic displacement parameters of neighbouring atoms.

In **1b**, ADDSYM suggests additional symmetry but the space group is confirmed as P_1. The EADP constraint was applied to the bridging hydrogen atoms of each borohydride moiety. All B-H distances were constrained to be equal within a standard uncertainty of 0.02 Å. H···H distances within the same BH_4 group were constrained to be equal within a standard uncertainty of 0.02 Å.

The H atoms of the two BH_4 groups in **1b and 3** were located in the Fourier difference map and their positions refined. The BH_4, H atoms could not be located in the residual electron density maps of **2** so they have been omitted from the structural model.

In **4**, the C10-C14 bond was fixed to 1.53(2) Å. The SIMU (su 0.04 A_2) and DELU (su 0.01 A_2) commands were applied to the atoms of the co-crystallised bipyridine solvent molecules to normalise the magnitude and direction of the atomic displacement parameters of neighbouring atoms. The SQUEEZE algorithm was used to account for residual electron density within the model attributed to highly disordered solvent within the voids.

Crystallography tables

[Th(Cl)$_2$(OTer^{Mes})$_2$DME].2PhMe ***1a.2PhMe***

Crystal data P13181 CCDC Number 1019326	
Chemical formula	$C_{80}H_{92}Cl_2O_4Th$
M_r	1420.48
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	170
a, *b*, *c* (Å)	18.6655 (8), 21.3909 (9), 19.2081 (10)
β (°)	109.480 (5)
V (Å^3)	7230.2 (6)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	2.18
Crystal size (mm)	1.05 × 0.73 × 0.54
Data collection	
Diffractometer	Xcalibur, Eos diffractometer
Absorption correction	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171 .NET) (compiled Oct 27 2011,15:02:11) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897)
T_{min}, T_{max}	0.663, 0.778
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	34187, 8282, 6690
R_{int}	0.059
(sin θ/λ)$_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.048, 0.122, 1.10
No. of reflections	8282
No. of parameters	378
No. of restraints	59
H-atom treatment	Riding
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.70, −0.88

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171 .NET) (compiled Oct 27 2011,15:02:11), *SIR92*, *SHELXL97* (Sheldrick, 2008), *ORTEP*, *Mercury*.

[Th(BH$_4$)$_2$(OTer^{Mes})$_2$DME].tol ***1b.PhMe***

Crystal data *PO14019* CCDC Number 1019327	
Chemical formula	$C_{59}H_{76}B_2O_4Th$
M_r	1102.85
Crystal system, space group	Triclinic, *P*1
Temperature (K)	120
a, *b*, *c* (Å)	8.3108 (2), 12.9109 (3), 12.9173 (2)
α, β, γ (°)	99.860 (2), 98.224 (2), 98.203 (2)
V (Å^3)	1331.50 (5)
Z	1
Radiation type	Cu *K*α
μ (mm^{-1})	9.36
Crystal size (mm)	0.08 × 0.04 × 0.02
Data collection	
Diffractometer	SuperNova (Cu) X-ray Source diffractometer
Absorption correction	Gaussian
T_{min}, T_{max}	0.584, 0.822
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22296, 8365, 8360
R_{int}	0.041
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.630
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.061, 1.05
No. of reflections	8365
No. of parameters	646
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$(\Delta/\sigma)_{max}$	0.143
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.28, −1.54
Absolute structure	Flack x determined using 2821 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	−0.007 (6)

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171 .NET) (compiled Oct 27 2011,15:02:11), *SIR92*, *SHELXL2014* (Sheldrick, 2014), *ORTEP*, *Mercury*.

[Th(BH$_4$)$_2$(OTer^{Mes})$_2$] ***2***

Crystal data *P14028d* CCDC Number 1019328	
Chemical formula	$C_{48}H_{50}B_2O_2Th$
M_r	912.54
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	170
a, *b*, *c* (Å)	22.1631 (18), 21.5236 (13), 10.9028 (8)
β (°)	122.674 (11)
V (Å^3)	4377.9 (7)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	3.44
Crystal size (mm)	0.44 × 0.06 × 0.05
Data collection	
Diffractometer	Xcalibur, Eos diffractometer
Absorption correction	Multi-scan
T_{min}, T_{max}	0.673, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	70166, 10027, 7268
R_{int}	0.115
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.092, 0.195, 1.23
No. of reflections	10027
No. of parameters	490
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0145P)^2 + 85.1623P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	3.44, −2.28

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171 .NET) (compiled Oct 27 2011,15:02:11), *SIR92*, *SHELXL2014* (Sheldrick, 2014), *ORTEP*, *Mercury*.

[Th(BH$_4$)$_2$(OTer^{Mes})$_2$(4,4 bipy)].2PhMe ***3.2PhMe***

Crystal data *P14040* CCDC Number 1019329	
Chemical formula	$C_{71.50}H_{78.50}B_2N_2O_2Th$
M_r	1251.52
Crystal system, space group	Triclinic, *P*1

Temperature (K)	170
a, *b*, *c* (Å)	12.9640 (2), 14.7824 (2), 17.7705 (3)
α, β, γ (°)	75.461 (1), 77.937 (1), 75.781 (1)
V (Å^3)	3155.84 (9)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	2.41
Crystal size (mm)	0.36 × 0.22 × 0.20
Data collection	
Diffractometer	Xcalibur, Eos diffractometer
Absorption correction	Multi-scan
T_{min}, T_{max}	0.926, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	87909, 14469, 13330
R_{int}	0.035
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.055, 1.07
No. of reflections	14469
No. of parameters	757
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.76, −0.51

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171 .NET) (compiled Oct 27 2011,15:02:11), *SIR92*, *SHELXL2014* (Sheldrick, 2014), *ORTEP*, *Mercury*.

[$ThCl_2(OTer^{Mes})_2$(4,4 bipy)].2(4,4 bipy).(C_6D_6) ***4.(C_6D_6).2(4,4 bipy)***

Crystal data *P14089b* CCDC number 1020471

Chemical formula	$C_{88.35}H_{83.35}Cl_2N_7O_2Th$
M_r	1578.18
Crystal system, space group	Triclinic, *P*1
Temperature (K)	170
a, *b*, *c* (Å)	13.342 (5), 14.040 (5), 23.743 (5)
α, β, γ (°)	95.480 (5), 104.752 (5), 110.128 (5)
V (Å^3)	3955 (2)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	2.00
Crystal size (mm)	0.54 × 0.05 × 0.04
Data collection	

Diffractometer	Xcalibur, Eos diffractometer
Absorption correction	Multi-scan
T_{min}, T_{max}	0.774, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	46423, 18134, 13670
R_{int}	0.050
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.124, 1.00
No. of reflections	18134
No. of parameters	886
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.61, −1.18

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171 .NET) (compiled Oct 27 2011,15:02:11), *SIR92*, *SHELXL2014* (Sheldrick, 2014), *ORTEP*, *Mercury*.

References

1. G. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112-122.
2. L. Palatinus and G. Chapuis, *J. Appl. Crystallogr.*, 2007, **40**, 786-790.
3. L. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837-838.