Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

2.2.2-Cryptand as a Bidentate Ligand in Rare-Earth Metal Chemistry

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Crystallographic Details for:

X-ray Data Collection, Structure Solution and Refinement for **1**, $[\{(R_2N)_2Ce(\text{crypt-}\kappa^2\text{-}O,O')\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ ($R = SiMe_3$).

A yellow crystal of approximate dimensions 0.164 x 0.187 x 0.335 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (120 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located about an inversion center. There were two molecules of diethylether solvent present.

Least-squares analysis yielded wR2 = 0.0984 and Goof = 1.041 for 474 variables refined against 13437 data (0.72 Å), R1 = 0.0387 for those 11059 data with $I > 2.0\sigma(I)$.

Table S1. Crystal data and structure refinement for **1**, $[\{(R_2N)_2Ce(\text{crypt-}\kappa^2\text{-}O,O')\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$

Identification code	abc16 (Amanda Chung)	
Empirical formula	$C_{60}\,H_{144}\,Ce_2\,N_{10}\,O_{12}\,Si_8 \bullet 2(C_4H_{10}O)$	
Formula weight	1851.04	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 12.8760(12) Å	a = 113.0740(14)°.
	b = 14.4999(14) Å	b = 92.3513(15)°.
	c = 15.4460(15) Å	g = 110.9522(14)°.
Volume	2421.9(4) $Å^3$	
Z	1	
Density (calculated)	1.269 Mg/m^3	
Absorption coefficient	1.082 mm^{-1}	
F(000)	982	
Crystal color	yellow	
Crystal size	0.335 x 0.187 x 0.164 mm^3	
Theta range for data collection	1.466 to 29.575°	
Index ranges	$-17 \le h \le 17$, $-20 \le k \le 18$, $-21 \le l \le 21$	

Reflections collected	32715
Independent reflections	13437 [R(int) = 0.0347]
Completeness to theta = 25.500°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7462 and 0.6682
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13437 / 0 / 474
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I) = 11059 data]	R1 = 0.0387, wR2 = 0.0898
R indices (all data, 0.72 Å)	R1 = 0.0546, wR2 = 0.0984
Largest diff. peak and hole	1.927 and -0.450 e.$Å^{-3}$

Table S2. Bond distances [Å] for **1**.

Ce(1)-N(3)	2.409(2)
Ce(1)-N(2)	2.411(2)
Ce(1)-N(1)	2.451(2)
Ce(1)-N(1)#1	2.468(2)
Ce(1)-O(2)	2.5453(18)
Ce(1)-O(1)	2.7957(18)
Si(1)-N(2)	1.712(2)
Si(1)-C(1)	1.868(3)
Si(1)-C(2)	1.882(3)
Si(1)-C(3)	1.886(3)
Si(2)-N(2)	1.709(2)
Si(2)-C(4)	1.874(3)
Si(2)-C(5)	1.876(3)
Si(2)-C(6)	1.879(3)
Si(3)-N(3)	1.704(2)
Si(3)-C(9)	1.874(3)
Si(3)-C(7)	1.881(3)
Si(3)-C(8)	1.885(3)
Si(4)-N(3)	1.712(2)
Si(4)-C(11)	1.878(3)
Si(4)-C(12)	1.878(3)
Si(4)-C(10)	1.882(3)

N(1)-N(1)#1	1.233(4)
N(1)-Ce(1)#1	2.468(2)
N(4)-C(19)	1.463(3)
N(4)-C(25)	1.466(4)
N(4)-C(13)	1.472(3)
N(5)-C(24)	1.460(4)
N(5)-C(30)	1.461(4)
N(5)-C(18)	1.477(4)
O(1)-C(15)	1.437(3)
O(1)-C(14)	1.439(3)
O(2)-C(16)	1.438(3)
O(2)-C(17)	1.443(3)
O(3)-C(21)	1.418(4)
O(3)-C(20)	1.422(4)
O(4)-C(22)	1.413(4)
O(4)-C(23)	1.418(4)
O(5)-C(27)	1.417(4)
O(5)-C(26)	1.424(4)
O(6)-C(29)	1.399(4)
O(6)-C(28)	1.413(4)
C(13)-C(14)	1.525(4)
C(15)-C(16)	1.485(4)
C(17)-C(18)	1.512(4)
C(19)-C(20)	1.504(4)
C(21)-C(22)	1.489(5)
C(23)-C(24)	1.507(5)
C(25)-C(26)	1.510(4)
C(27)-C(28)	1.495(5)
C(29)-C(30)	1.525(5)
O(7)-C(33)	1.394(5)
O(7)-C(32)	1.413(5)
C(31)-C(32)	1.490(7)
C(33)-C(34)	1.454(7)

Table S3. Bond angles [˚] for **1**.

N(3)-Ce(1)-N(2)	123.09(7)
N(3)-Ce(1)-N(1)	104.41(7)
N(2)-Ce(1)-N(1)	116.01(7)
N(3)-Ce(1)-N(1)#1	102.44(7)
N(2)-Ce(1)-N(1)#1	95.60(7)
N(1)-Ce(1)-N(1)#1	29.04(9)
N(3)-Ce(1)-O(2)	129.31(7)
N(2)-Ce(1)-O(2)	99.09(7)
N(1)-Ce(1)-O(2)	76.30(6)
N(1)#1-Ce(1)-O(2)	99.65(7)
N(3)-Ce(1)-O(1)	92.74(6)
N(2)-Ce(1)-O(1)	84.78(6)
N(1)-Ce(1)-O(1)	136.28(6)
N(1)#1-Ce(1)-O(1)	161.42(6)
O(2)-Ce(1)-O(1)	62.08(6)
N(2)-Si(1)-C(1)	111.77(13)
N(2)-Si(1)-C(2)	109.60(12)
C(1)-Si(1)-C(2)	109.47(14)
N(2)-Si(1)-C(3)	115.90(13)
C(1)-Si(1)-C(3)	106.01(15)
C(2)-Si(1)-C(3)	103.66(14)
N(2)-Si(2)-C(4)	111.74(12)
N(2)-Si(2)-C(5)	113.80(13)
C(4)-Si(2)-C(5)	105.34(13)
N(2)-Si(2)-C(6)	113.00(13)
C(4)-Si(2)-C(6)	104.82(14)
C(5)-Si(2)-C(6)	107.46(16)
N(3)-Si(3)-C(9)	112.62(13)
N(3)-Si(3)-C(7)	114.88(12)
C(9)-Si(3)-C(7)	105.04(13)
N(3)-Si(3)-C(8)	110.00(12)
C(9)-Si(3)-C(8)	107.59(13)
C(7)-Si(3)-C(8)	106.24(13)
N(3)-Si(4)-C(11)	115.86(13)
N(3)-Si(4)-C(12)	107.83(12)

C(11)-Si(4)-C(12)	105.67(14)
N(3)-Si(4)-C(10)	114.97(13)
C(11)-Si(4)-C(10)	102.98(15)
C(12)-Si(4)-C(10)	109.01(15)
N(1)#1-N(1)-Ce(1)	76.3(2)
N(1)#1-N(1)-Ce(1)#1	74.7(2)
Ce(1)-N(1)-Ce(1)#1	150.96(9)
Si(2)-N(2)-Si(1)	119.82(12)
Si(2)-N(2)-Ce(1)	121.97(11)
Si(1)-N(2)-Ce(1)	118.10(11)
Si(3)-N(3)-Si(4)	123.54(13)
Si(3)-N(3)-Ce(1)	120.24(11)
Si(4)-N(3)-Ce(1)	116.21(11)
C(19)-N(4)-C(25)	110.4(2)
C(19)-N(4)-C(13)	112.7(2)
C(25)-N(4)-C(13)	109.1(2)
C(24)-N(5)-C(30)	112.0(2)
C(24)-N(5)-C(18)	112.4(3)
C(30)-N(5)-C(18)	111.0(3)
C(15)-O(1)-C(14)	112.0(2)
C(15)-O(1)-Ce(1)	113.58(15)
C(14)-O(1)-Ce(1)	127.71(14)
C(16)-O(2)-C(17)	115.2(2)
C(16)-O(2)-Ce(1)	108.25(15)
C(17)-O(2)-Ce(1)	131.86(16)
C(21)-O(3)-C(20)	112.0(3)
C(22)-O(4)-C(23)	112.2(3)
C(27)-O(5)-C(26)	110.8(2)
C(29)-O(6)-C(28)	113.0(2)
N(4)-C(13)-C(14)	111.2(2)
O(1)-C(14)-C(13)	113.3(2)
O(1)-C(15)-C(16)	107.2(2)
O(2)-C(16)-C(15)	109.1(2)
O(2)-C(17)-C(18)	112.8(2)
N(5)-C(18)-C(17)	114.2(3)
N(4)-C(19)-C(20)	114.5(2)

O(3)-C(20)-C(19)	110.2(2)
O(3)-C(21)-C(22)	110.6(3)
O(4)-C(22)-C(21)	110.9(3)
O(4)-C(23)-C(24)	109.9(2)
N(5)-C(24)-C(23)	113.1(3)
N(4)-C(25)-C(26)	113.1(2)
O(5)-C(26)-C(25)	109.3(2)
O(5)-C(27)-C(28)	111.2(3)
O(6)-C(28)-C(27)	115.4(3)
O(6)-C(29)-C(30)	107.5(2)
N(5)-C(30)-C(29)	110.0(3)
C(33)-O(7)-C(32)	115.1(4)
O(7)-C(32)-C(31)	109.5(4)
O(7)-C(33)-C(34)	111.8(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1

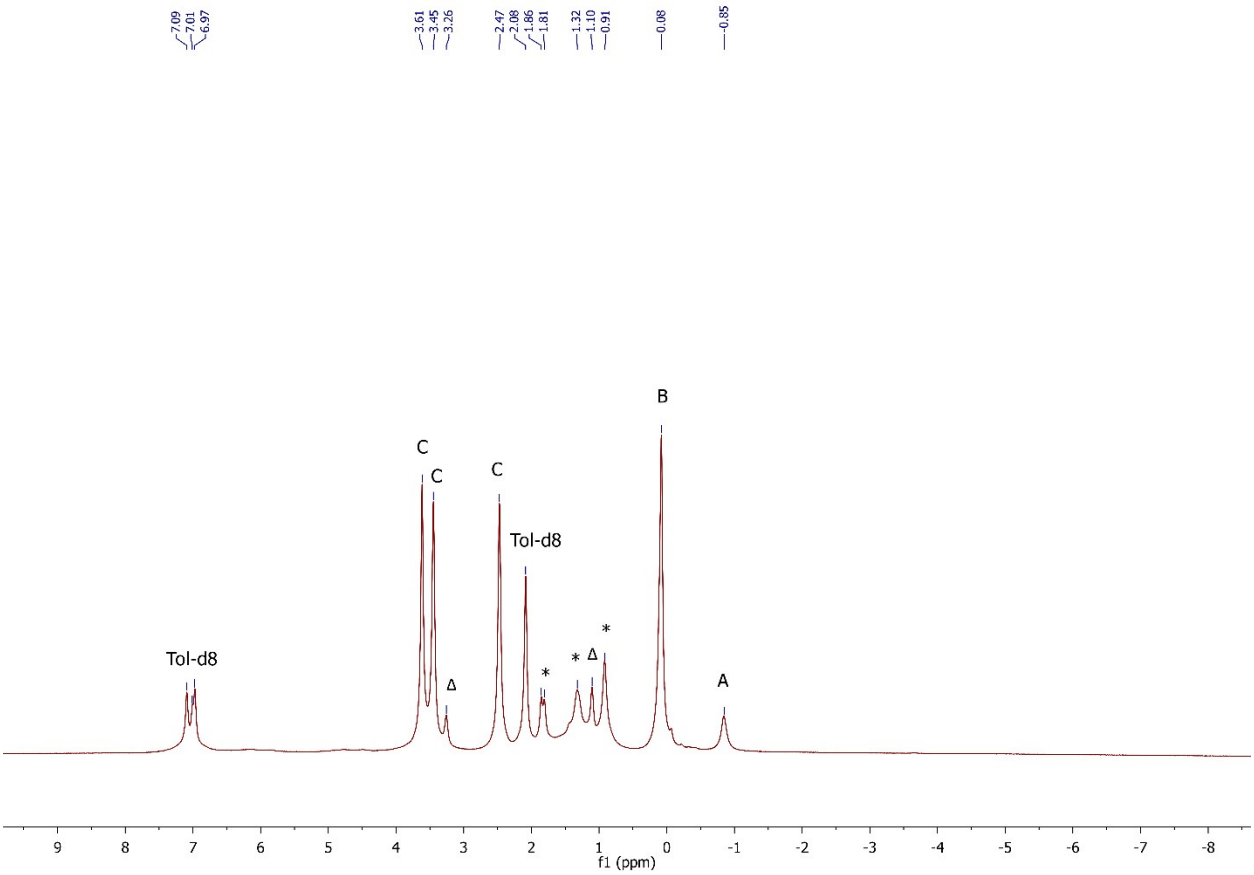

Figure S1. ^{1}H NMR spectrum of **1** in toluene-d_8. A: Si*Me*$_3$ of **1**; B: HN*; C: crypt; Δ: diethyl ether; *unidentified.

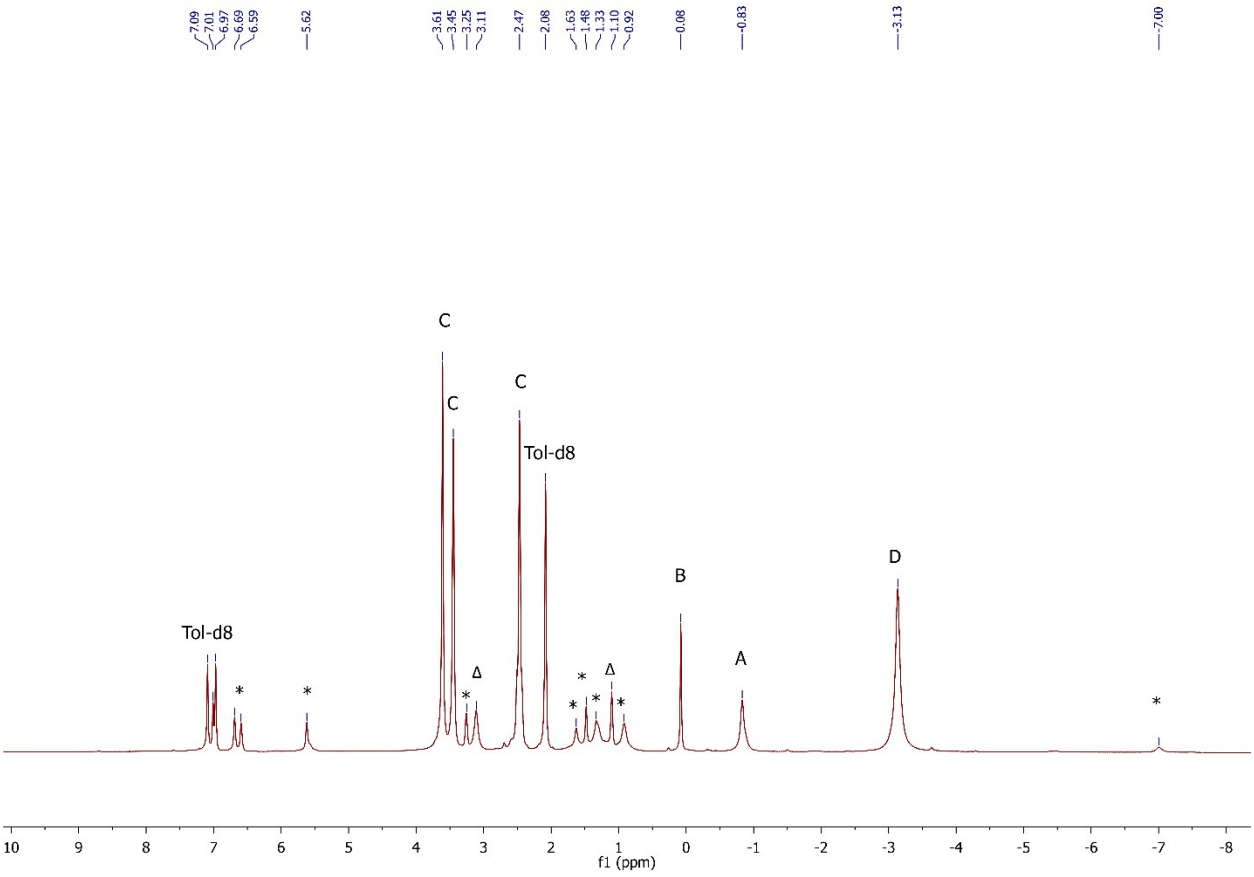

Figure S2. ^{1}H NMR spectrum of **1** reaction mixture in toluene-d_8. A: Si*Me*$_3$ of **1**; B: HN*; C: crypt; D: Si*Me*$_3$ of $Ce(NR_2)_3$; Δ: diethyl ether; *unidentified.

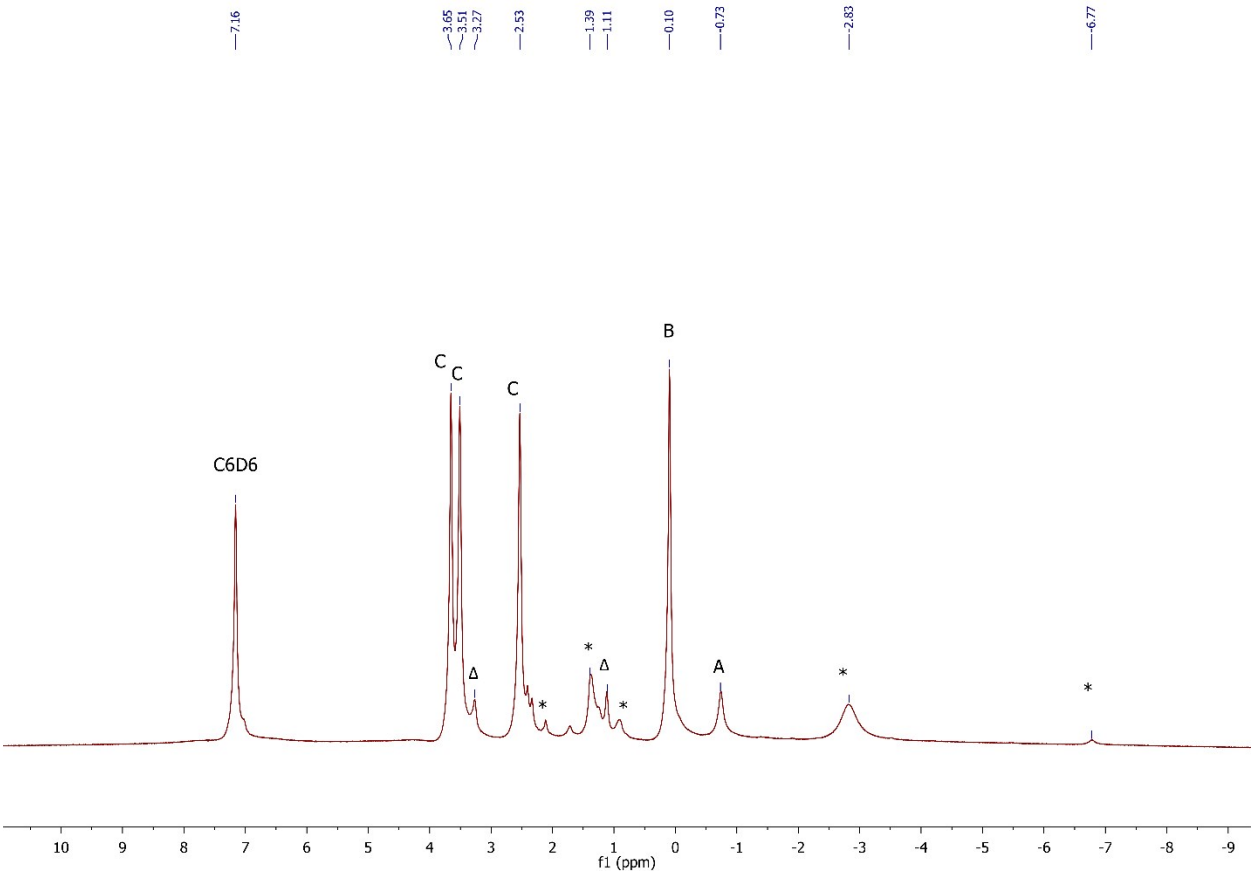

Figure S3. ^{1}H NMR spectrum of **1** reaction mixture in C_6D_6. A: Si*Me*$_3$ of **1**; B: HN*; C: crypt; Δ: diethyl ether; *unidentified.

X-ray Data Collection, Structure Solution and Refinement for **2**, $(C_5Me_5)_2Yb(crypt\text{-}\kappa^2\text{-}O,O')$.

A green crystal of approximate dimensions 0.051 x 0.072 x 0.149 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space groups *Pbcm* and $Pca2_1$. It was later determined that space group $Pca2_1$ was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis.

Hydrogen atoms were included using a riding model. There were two molecules of the formula-unit present.

Least-squares analysis yielded wR2 = 0.1128 and Goof = 1.059 for 488 variables refined against 14833 data (0.80 Å), R1 = 0.0649 for those 10306 data with $I > 2.0\sigma(I)$. The structure was refined as a two-component twin, however, it appeared that non-merohedral twinning may have been present. Unfortunately, the frame data was not available to investigate this further.

Table S4. Crystal data and structure refinement for **2,** $(C_5Me_5)_2Yb(crypt\text{-}\kappa^2\text{-}O,O')$.

Identification code	dnh29 (Dan Huh)	
Empirical formula	$C_{38}\ H_{66}\ N_2\ O_6\ Yb$	
Formula weight	819.96	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pca2_1$	
Unit cell dimensions	a = 26.384(4) Å	a = 90°.
	b = 9.3048(14) Å	b = 90°.
	c = 31.544(5) Å	g = 90°.
Volume	7744(2) $Å^3$	
Z	8	
Density (calculated)	1.407 Mg/m^3	
Absorption coefficient	2.460 mm^{-1}	
F(000)	3408	
Crystal color	green	
Crystal size	0.149 x 0.072 x 0.051 mm^3	
Theta range for data collection	1.291 to 26.408°	

Index ranges	$-32 \leq h \leq 33$, $-11 \leq k \leq 11$, $-39 \leq l \leq 39$
Reflections collected	70551
Independent reflections	14833 [R(int) = 0.1518]
Completeness to theta = 25.500°	94.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.3742
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14833 / 1 / 488
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I) = 10306 data]	R1 = 0.0649, wR2 = 0.1017
R indices (all data, 0.80 Å)	R1 = 0.1059, wR2 = 0.1128
Largest diff. peak and hole	1.230 and -1.329 e.$Å^{-3}$

References.

1. APEX2 Version 2014.11-0, Bruker AXS, Inc.; Madison, WI 2014.

2. SAINT Version 8.34a, Bruker AXS, Inc.; Madison, WI 2013.

3. Sheldrick, G. M. SADABS, Version 2014/5, Bruker AXS, Inc.; Madison, WI 2014.

4. Sheldrick, G. M. SHELXTL, Version 2014/7, Bruker AXS, Inc.; Madison, WI 2014.

5. International Tables for Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.

Definitions:

$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

$Goof = S = [\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.