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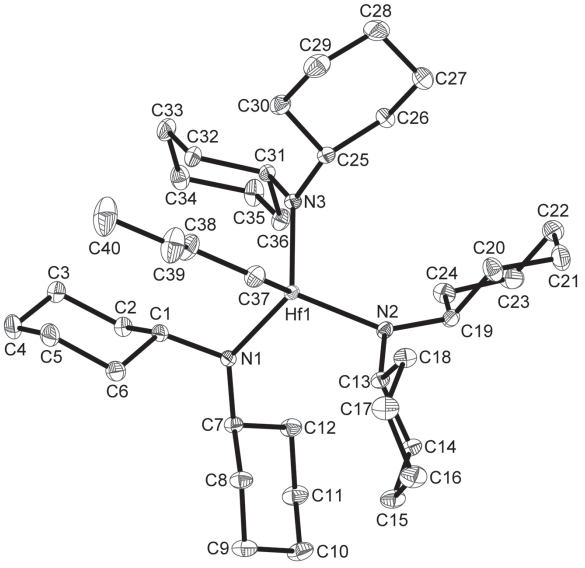
Crystal structure of *n*-butyl-tris(dicyclohexylamido)hafnium(IV), $C_{40}H_{75}HfN_3$



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Abstract

$C_{40}H_{75}HfN_3$, monoclinic, $P2_1/n$ (no. 14), $a = 10.7446(3)$ Å, $b = 13.6547(4)$ Å, $c = 26.5464(9)$ Å, $\beta = 92.2375(15)°$, $V = 3891.8(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0195$, $wR_{ref}(F^2) = 0.0461$, $T = 100(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure (hydrogen atoms are omitted for clarity). Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.36 \times 0.36 \times 0.32$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	27.1 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	76°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	225553, 20900, 0.022
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 19301
$N(param)_{refined}$:	398
Programs:	SHELX [1], Bruker programs [2]

Source of material

All reactions were carried out under a dry nitrogen atmosphere using Schlenk-technique. Tris(dicyclohexylamido) hafnium(IV) chloride is easily available by a literature known synthesis [3]. The reaction with *n*-butyllithium was carried out according to the procedure known for the analogous zirconium complex [4]. To a solution of $(Cy_2N)_3HfCl$ (500 mg, 0.662 mmol) in 20 mL *n*-hexane was added a *n*-butyllithium solution in *n*-hexane (0.27 mL, 0.662 mmol, 2.5 mol/l). The resulting mixture was stirred at ambient temperature. The mixture was filtered over a pad of celite and concetrated to 10 mL. Colourless crystals were obtained from this solution at −30 °C after three days, identified as the title compound *n*-butyl-tris(dicyclohexylamido)hafnium(IV).

Experimental details

All hydrogen atoms were located in the difference Fourier syntheses, and subsequently fixed to geometric positions using appropiate riding models.

Comment

The title compound is a rare example of a structural characterized hafnium complex with a terminal *n*-butyl group. The complex *n*-$BuHf(NCy_2)_3$ is the first structural characterized hafnium-*n*-butyl complex employing three amido ligands at the electron deficient metal center. It is isostructural to the analogous zirconium compound [4]. There are only three other examples for related hafnium complexes listed in the Cambridge Crystallographic Database [5–7].

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Hf1	0.41335(2)	0.76960(2)	0.11955(2)	0.00992(1)
N1	0.47000(7)	0.62661(6)	0.12569(3)	0.01208(13)
N2	0.22680(8)	0.78168(6)	0.10233(3)	0.01219(13)
N3	0.46600(8)	0.85440(6)	0.18020(3)	0.01237(13)
C1	0.60777(9)	0.62364(7)	0.12819(4)	0.01329(15)
H1	0.6361	0.6932	0.1312	0.016*
C2	0.66360(9)	0.57003(8)	0.17489(4)	0.01623(16)
H2A	0.6271	0.5971	0.2056	0.019*
H2B	0.6416	0.4997	0.1728	0.019*
C3	0.80570(10)	0.58074(9)	0.17898(5)	0.0212(2)
H3A	0.8274	0.6503	0.1849	0.025*
H3B	0.8387	0.5423	0.2082	0.025*
C4	0.86654(11)	0.54538(10)	0.13121(5)	0.0247(2)
H4A	0.9570	0.5594	0.1338	0.030*
H4B	0.8556	0.4736	0.1279	0.030*
C5	0.80913(11)	0.59594(9)	0.08458(5)	0.0221(2)
H5A	0.8461	0.5686	0.0540	0.027*
H5B	0.8288	0.6667	0.0860	0.027*
C6	0.66744(10)	0.58236(9)	0.08089(4)	0.01835(18)
H6A	0.6474	0.5118	0.0775	0.022*
H6B	0.6328	0.6166	0.0506	0.022*
C7	0.40903(9)	0.53027(7)	0.12424(4)	0.01355(15)
H7	0.4710	0.4811	0.1375	0.016*
C8	0.36691(10)	0.49809(8)	0.07081(4)	0.01663(17)
H8A	0.3059	0.5459	0.0565	0.020*
H8B	0.4396	0.4974	0.0490	0.020*
C9	0.30760(12)	0.39625(9)	0.07093(4)	0.02057(19)
H9A	0.2774	0.3794	0.0363	0.025*
H9B	0.3712	0.3473	0.0817	0.025*
C10	0.19903(12)	0.39196(9)	0.10627(5)	0.0227(2)
H10A	0.1682	0.3238	0.1080	0.027*
H10B	0.1302	0.4334	0.0925	0.027*
C11	0.23708(12)	0.42695(9)	0.15927(4)	0.0212(2)
H11A	0.2962	0.3794	0.1751	0.025*
H11B	0.1625	0.4295	0.1800	0.025*
C12	0.29799(10)	0.52817(8)	0.15863(4)	0.01693(17)
H12A	0.3264	0.5462	0.1933	0.020*
H12B	0.2357	0.5772	0.1468	0.020*
C13	0.21032(9)	0.75034(7)	0.04917(4)	0.01308(15)
H13	0.2895	0.7163	0.0411	0.016*
C14	0.10656(10)	0.67473(8)	0.03891(4)	0.01632(16)
H14A	0.1155	0.6206	0.0636	0.020*
H14B	0.0245	0.7060	0.0432	0.020*
C15	0.11261(12)	0.63366(9)	−0.01464(4)	0.0212(2)
H15A	0.1913	0.5969	−0.0177	0.025*
H15B	0.0427	0.5875	−0.0209	0.025*
C16	0.10565(13)	0.71478(10)	−0.05421(5)	0.0248(2)
H16A	0.0220	0.7452	−0.0546	0.030*
H16B	0.1179	0.6862	−0.0879	0.030*
C17	0.20469(13)	0.79331(10)	−0.04327(4)	0.0231(2)
H17A	0.2885	0.7649	−0.0472	0.028*
H17B	0.1936	0.8475	−0.0678	0.028*
C18	0.19518(11)	0.83334(8)	0.01023(4)	0.01709(17)
H18A	0.1132	0.8653	0.0136	0.021*
H18B	0.2607	0.8832	0.0167	0.021*

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C19	0.11512(9)	0.81571(8)	0.12730(4)	0.01483(15)
H19	0.0432	0.7752	0.1145	0.018*
C20	0.08316(11)	0.92372(9)	0.11686(4)	0.02080(19)
H20A	0.1549	0.9651	0.1278	0.025*
H20B	0.0683	0.9332	0.0801	0.025*
C21	−0.03235(12)	0.95645(11)	0.14440(5)	0.0276(3)
H21A	−0.0492	1.0264	0.1371	0.033*
H21B	−0.1054	0.9180	0.1320	0.033*
C22	−0.01346(11)	0.94214(10)	0.20110(5)	0.0238(2)
H22A	−0.0906	0.9605	0.2180	0.029*
H22B	0.0545	0.9853	0.2141	0.029*
C23	0.01906(12)	0.83571(10)	0.21313(5)	0.0249(2)
H23A	−0.0542	0.7940	0.2046	0.030*
H23B	0.0382	0.8293	0.2498	0.030*
C24	0.13045(11)	0.79887(8)	0.18427(4)	0.01809(17)
H24A	0.1416	0.7279	0.1907	0.022*
H24B	0.2067	0.8328	0.1971	0.022*
C25	0.44877(9)	0.95792(7)	0.16540(4)	0.01409(15)
H25	0.4039	0.9567	0.1317	0.017*
C26	0.36608(10)	1.01802(8)	0.19989(5)	0.01922(18)
H26A	0.2868	0.9827	0.2044	0.023*
H26B	0.4086	1.0253	0.2334	0.023*
C27	0.33837(12)	1.11967(9)	0.17762(6)	0.0267(2)
H27A	0.2891	1.1126	0.1455	0.032*
H27B	0.2882	1.1577	0.2012	0.032*
C28	0.45894(13)	1.17459(9)	0.16809(6)	0.0289(3)
H28A	0.4389	1.2380	0.1516	0.035*
H28B	0.5033	1.1884	0.2007	0.035*
C29	0.54318(13)	1.11567(10)	0.13491(5)	0.0259(2)
H29A	0.6225	1.1513	0.1311	0.031*
H29B	0.5027	1.1078	0.1010	0.031*
C30	0.57017(10)	1.01465(8)	0.15781(4)	0.01818(17)
H30A	0.6159	1.0224	0.1907	0.022*
H30B	0.6236	0.9770	0.1352	0.022*
C31	0.51963(9)	0.83741(7)	0.23106(4)	0.01325(15)
H31	0.5051	0.8976	0.2514	0.016*
C32	0.66064(9)	0.81862(8)	0.23196(4)	0.01644(16)
H32A	0.6780	0.7625	0.2097	0.020*
H32B	0.7031	0.8769	0.2186	0.020*
C33	0.71334(10)	0.79679(10)	0.28522(5)	0.02072(19)
H33A	0.8031	0.7813	0.2838	0.025*
H33B	0.7048	0.8556	0.3066	0.025*
C34	0.64561(11)	0.71081(9)	0.30888(4)	0.02002(19)
H34A	0.6614	0.6503	0.2896	0.024*
H34B	0.6781	0.7009	0.3439	0.024*
C35	0.50579(11)	0.73036(10)	0.30892(4)	0.0213(2)
H35A	0.4898	0.7867	0.3312	0.026*
H35B	0.4631	0.6724	0.3225	0.026*
C36	0.45243(10)	0.75231(8)	0.25595(4)	0.01631(16)
H36A	0.3629	0.7685	0.2578	0.020*
H36B	0.4595	0.6930	0.2348	0.020*
C37	0.50835(10)	0.83298(8)	0.05218(4)	0.01800(17)
H37A	0.4786	0.7940	0.0227	0.022*
H37B	0.4737	0.8996	0.0472	0.022*
C38	0.64836(11)	0.84276(11)	0.04786(5)	0.0240(2)
H38A	0.6869	0.7777	0.0537	0.029*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H38B	0.6806	0.8870	0.0749	0.029*
C39	0.68963(13)	0.88184(13)	−0.00260(6)	0.0342(3)
H39A	0.6572	0.8383	−0.0299	0.041*
H39B	0.6530	0.9476	−0.0084	0.041*
C40	0.83016(14)	0.88879(14)	−0.00522(8)	0.0417(4)
H40A	0.8517	0.9132	−0.0385	0.063*
H40B	0.8670	0.8238	0.0003	0.063*
H40C	0.8625	0.9339	0.0209	0.063*

One of them is the recently published crystal structure of Di-*n*-butylbis(η^5-pentamethyl-cyclopentadienyl)hafnium(IV) [5]. Di-*n*-butylbis(η^5-cyclopentadienyl)hafnium(IV) ($Cp_2Hf(n\text{-}Bu)_2$) is known and used as a Hf(II) source at elevated temperatures (100 °C), analogues to the Negishi System Cp_2ZrCl_2/*n*-BuLi which eliminates butane and 1-butene to give the free metallocene [8, 9]. Analogous to $Cp_2Hf(n\text{-}Bu)_2$ the complex $n\text{-}BuHf(NCy_2)_3$ is remarkably robust. There are no hints for a β-agostic interaction in the molecular structure. The angle Hf(1)-C(37)-C(38) is 124.84(8)° and thereby within the range for non-agostic compounds [10, 11]. The metal-carbon σ-bond Hf(1)-C(37) (2.2653(11) Å) is within the expected range for such a bond. The hafnium-nitrogen bonds are very similar (Hf(1)-N(1) 2.0497(8) Å, Hf(1)-N(2) 2.0450(8) Å, Hf(1)-N(3) 2.0451(8) Å). These bond lengths are shortened in comparison to a typical single bond due to attractive interactions between the nitrogen lone pair and the electron deficient metal center [12]. All nitrogen atoms are coordinated trigonal planar (sum of all angles: N1 359.8°, N2 359.9°, N3 359.9°).

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