Crystal structure of (18-crown-6)bis(tetrahydrofuran)potassium bis(2,3,4,5-tetramethylphospholy)bis(borohydride)neodymium(III), $[K(C_{12}H_{24}O_6)(C_4H_8O)_2]\{[C_4(CH_3)_4P]_2Nd(BH_4)_2\}$

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Abstract

$C_{36}H_{72}B_2KNdO_8P_2$, triclinic, $P\bar{1}$ (No. 2), $a = 10.489(2)$ Å, $b = 11.784(2)$ Å, $c = 19.103(4)$ Å, $\alpha = 98.29(3)^\circ$, $\beta = 94.07(3)^\circ$, $\gamma = 104.26(3)^\circ$, $V = 2250.5$ Å³, $Z = 2$, $R_{\text{int}}(F) = 0.069$, $wR_{\text{ref}}(F^2) = 0.194$, $T = 123$ K.

Source of material

Addition of 18-crown-6 (1.7 equivalents, 143 μ mol) to a THF (20 mL) solution of $[K(THF)][Nd(PC_4Me_4)_2(BH_4)_2]$ (47.3 mg, 84 μ mol) quantitatively gave the title compound. The product was recrystallized from a THF-pentane mixture to afford light blue crystals within 7 days. The sample was also characterized by NMR and IR spectroscopy. Spectroscopic data are included in the deposited CIF-file.

Experimental details

Hydrogen atoms (except H atoms of BH_4) were introduced at calculated positions as riding atoms, with an isotropic displacement parameter equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the parent atom. The hydrogen atoms of BH_4 were not found.

Discussion

Organometallic borohydrides complexes of neodymium are quite rare [1,5]. Bisborohydride derivatives include the cyclopentadienyl substituted species $(C_5H^iPr_4)Nd(BH_4)_2$ [1] and $[K(18\text{-crown-6})\{(C_{13}H_8)CPh_2(C_5H_4)Nd(BH_4)_2\}]_2$ [3] while the monoborohydride compounds, in addition to $(C_5H_4CH_2CH_2OMe)_2Nd(BH_4)$ [4], are essentially limited to the cyclooctatetraenyl derivatives $(\eta\text{-}C_8H_8)Nd(BH_4)(THF)_2$ and

$(\eta\text{-}C_5Me_5)Nd(BH_4)_2(THF)_2$ [2,5]. Such borohydrides of neodymium(III) revealed themselves as versatile precursors for the synthesis of previously inaccessible compounds such as the cationic derivatives $[(\eta\text{-}C_8H_8)Nd(L)_x][BPh_4]$ ($L = THF_4$, $HMPA_3$) [5,6]. Although a few bis(phospholy)lanthanide(III) examples are known [7,8], the complex we isolated, $[K(THF)][(PC_4Me_4)_2Nd(BH_4)_2]$ [2], is the first mixed borohydride-phospholy derivative of a 4f element. Addition of a crown ether to that product allowed the synthesis of the parent complex $[K(18\text{-crown-6})(THF)_2][(PC_4Me_4)_2Nd(BH_4)_2]$, the crystal structure of which has been determined and that is reported in this paper.

The structure of $[K(18\text{-crown-6})(THF)_2][(PC_4Me_4)_2Nd(BH_4)_2]$ reveals molecular cation and anion pairs. The figure shows the molecular anion. The potassium ion, which is encapsulated into the crown ether and surrounded by two coordinated THF, displays the expected coordination. The molecular anion adopts a distorted tetrahedral configuration with the following relevant angles $\angle B1\text{-Nd-B2} = 98.7(3)^\circ$, $\angle P1\text{-Nd-P2} = 128.7(7)^\circ$ and the mean value for $\angle B\text{-Nd-P}^* = 106.3(7)^\circ$, ranging from $105.6(2)$ to $107.3(2)^\circ$ (P^* = phospholy centroid). The phospholy ligands are bound to the metal in an η^5 mode. Both phospholy rings are planar (within 0.031 Å and 0.021 Å for phospholyls "P1" and "P2" respectively) with average Nd—C bond distance of 2.87(2) Å, Nd—P1 and Nd—P2 bond distances of 2.982(3) Å and 2.995(3) Å and Nd-phospholy centroid of 2.579(3) Å and 2.595(3) Å for "P1" and "P2", respectively. These distances are comparable to those observed in the only other crystallographically characterized bisphospholy lanthanide(III) complex, $[(\eta^5\text{-}C_4Me_4P)Sm(\mu_3\text{-Cl})_2(\mu\text{-}\eta^5\text{-}C_4Me_4P)K(Et_2O)]_\infty$, ($d(Sm\text{-}C) = 2.78(2)$ Å, $d(Sm\text{-}P) = 2.916(11)$ Å) [9]. The Nd-borohydride ligands distances ranging from 2.588(7) Å to 2.670(5) Å and averaging to 2.63(5) Å agree well with the short distances observed for a tridentate binding mode of the BH_4 ligand in $(C_5H^iPr_4)Nd(BH_4)_2$ (mean $d(Nd\text{-}B) = 2.600(8)$ Å) [1], $(C_5H_4CH_2CH_2OMe)_2Nd(BH_4)$ (2.664(25) Å) [4] or in $[K(18\text{-crown-6})\{(C_{13}H_8)CPh_2(C_5H_4)Nd(BH_4)_2\}]_2 \cdot C_4H_8O_2$ (mean $d(Nd\text{-}B) = 2.632(9)$ Å) [3]. This value is however much shorter than that measured in the dimeric complex $[(\eta\text{-}C_8H_8)Nd(\mu_3\text{-H})_2B(\mu_2\text{-H})_2(THF)]_2$ (2.875(6) Å and 2.941(6) Å) [5]. The infrared data of our complex confirm the tridentate binding mode observed crystallographically [10,11].

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Table 1. Data collection and handling.

Crystal:	sky-blue, irregular, size 0.06 × 0.10 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	13.60 cm ⁻¹
Diffractionmeter, scan mode:	Nonius Kappa-CCD, $\Delta\phi = 2^\circ$
$2\theta_{\max}$:	49.34°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	13567, 7004
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 4318
$N(\text{param})_{\text{refined}}$:	454
Program:	SHELXTL [12]

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(16B)	2i	0.2318	0.8891	0.7065	0.079
H(16C)	2i	0.2869	1.0215	0.7442	0.079
H(17A)	2i	0.6571	0.2679	0.5875	0.062
H(17B)	2i	0.6512	0.3622	0.5376	0.062
H(18A)	2i	0.7084	0.2236	0.4457	0.064
H(18B)	2i	0.7261	0.1389	0.5001	0.064
H(19A)	2i	0.9536	0.1790	0.4826	0.065
H(19B)	2i	0.8600	0.1106	0.4135	0.065
H(20A)	2i	1.0177	0.1916	0.3373	0.062
H(20B)	2i	1.1154	0.2517	0.4063	0.062
H(21A)	2i	1.1630	0.3516	0.3079	0.060
H(21B)	2i	1.0269	0.3849	0.3114	0.060
H(22A)	2i	1.1763	0.5916	0.3353	0.063
H(22B)	2i	1.3031	0.5440	0.3431	0.063
H(23A)	2i	1.0371	0.3101	0.6207	0.081
H(23B)	2i	1.1390	0.4150	0.6723	0.081
H(24A)	2i	1.1905	0.2078	0.5998	0.116
H(24B)	2i	1.2360	0.2653	0.6804	0.116
H(25A)	2i	1.4000	0.3060	0.5874	0.096
H(25B)	2i	1.4055	0.4066	0.6528	0.096
H(26A)	2i	1.3464	0.5139	0.5724	0.096
H(26B)	2i	1.3074	0.4020	0.5114	0.096
H(27A)	2i	1.1868	0.8090	0.8920	0.062
H(27B)	2i	1.0860	0.8132	0.9489	0.062
H(28A)	2i	1.2534	0.8014	1.0422	0.058
H(28B)	2i	1.3516	0.8048	0.9835	0.058
H(29A)	2i	1.3676	0.6152	0.9992	0.061
H(29B)	2i	1.4215	0.7096	1.0685	0.061
H(30A)	2i	1.3822	0.5512	1.1336	0.057
H(30B)	2i	1.3166	0.4567	1.0657	0.057
H(31A)	2i	1.2371	0.4001	1.1740	0.064
H(31B)	2i	1.1720	0.5075	1.1806	0.064
H(32A)	2i	0.9570	0.3701	1.1705	0.066
H(32B)	2i	1.0277	0.2664	1.1659	0.066
H(33A)	2i	0.8769	0.6151	1.1816	0.077
H(33B)	2i	0.7855	0.5144	1.1232	0.077
H(34A)	2i	0.6444	0.6246	1.1032	0.114
H(34B)	2i	0.6893	0.6724	1.1851	0.114
H(35A)	2i	0.8302	0.8352	1.1647	0.115
H(35B)	2i	0.7279	0.8149	1.0966	0.115
H(36A)	2i	0.8656	0.7560	1.0249	0.085
H(36B)	2i	0.9772	0.8142	1.0887	0.085

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(5A)	2i	0.6400	0.9388	0.5002	0.076
H(5B)	2i	0.5445	0.8428	0.5344	0.076
H(5C)	2i	0.6976	0.8575	0.5448	0.076
H(6A)	2i	0.9249	1.0950	0.5960	0.080
H(6B)	2i	0.8889	0.9614	0.6056	0.080
H(6C)	2i	0.9572	1.0608	0.6703	0.080
H(7A)	2i	0.8895	1.2887	0.7363	0.082
H(7B)	2i	0.9283	1.1795	0.7613	0.082
H(7C)	2i	0.8294	1.2380	0.8017	0.082
H(8A)	2i	0.5683	1.2972	0.7367	0.084
H(8B)	2i	0.6188	1.2487	0.8027	0.084
H(8C)	2i	0.4735	1.1943	0.7662	0.084
H(13A)	2i	0.5966	0.8838	0.9892	0.087
H(13B)	2i	0.7006	0.9722	0.9545	0.087
H(13C)	2i	0.6874	0.8354	0.9372	0.087
H(14A)	2i	0.4411	0.6250	0.8840	0.095
H(14B)	2i	0.5876	0.6681	0.8670	0.095
H(14C)	2i	0.4748	0.6053	0.8052	0.095
H(15A)	2i	0.2070	0.6482	0.7602	0.093
H(15B)	2i	0.3314	0.6197	0.7282	0.093
H(15C)	2i	0.2584	0.7031	0.6942	0.093
H(16A)	2i	0.1798	0.9337	0.7776	0.079

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd	2i	0.61753(5)	0.91132(5)	0.74440(3)	0.0382(3)	0.0441(3)	0.0417(3)	0.0040(2)	0.0128(2)	0.0137(2)
K(1)	1g	0	1/2	1/2	0.064(2)	0.068(2)	0.063(2)	0.009(2)	0.016(2)	0.015(2)
K(2)	1c	0	1/2	0	0.059(2)	0.067(2)	0.058(2)	0.011(2)	0.016(2)	0.017(2)
P(1)	2i	0.5046(3)	1.0345(3)	0.6393(1)	0.044(2)	0.055(2)	0.044(2)	0.004(1)	0.008(1)	0.017(1)
P(2)	2i	0.4770(3)	1.0016(2)	0.8628(1)	0.049(2)	0.051(2)	0.043(2)	0.006(1)	0.013(1)	0.013(1)
O(1)	2i	0.8155(6)	0.3089(6)	0.5368(4)	0.043(4)	0.052(4)	0.054(4)	0.000(3)	0.016(3)	0.005(4)
O(2)	2i	0.9370(6)	0.2794(6)	0.4106(4)	0.039(4)	0.060(4)	0.048(4)	0.004(3)	0.012(3)	0.012(4)
O(3)	2i	1.1584(6)	0.4651(6)	0.3942(3)	0.045(4)	0.057(4)	0.042(4)	0.005(3)	0.017(3)	0.014(3)
O(4)	2i	1.1616(8)	0.4172(8)	0.5700(5)	0.058(5)	0.103(7)	0.079(6)	0.001(5)	0.021(4)	0.035(5)
O(6)	2i	1.1765(6)	0.6865(6)	0.9525(3)	0.040(4)	0.049(4)	0.052(4)	0.003(3)	0.009(3)	0.015(4)
O(7)	2i	1.2487(6)	0.5993(6)	1.0750(3)	0.036(4)	0.049(4)	0.052(4)	0.002(3)	0.013(3)	0.008(3)
O(8)	2i	1.0895(6)	0.3805(6)	1.1005(3)	0.042(4)	0.051(4)	0.036(4)	-0.004(3)	0.010(3)	0.017(3)
O(9)	2i	0.9053(8)	0.6391(8)	1.0839(4)	0.069(5)	0.076(6)	0.080(6)	0.020(5)	0.030(5)	0.034(5)
C(1)	2i	0.641(1)	0.9881(9)	0.6069(5)	0.044(6)	0.044(6)	0.044(6)	0.000(5)	0.005(5)	0.003(5)
C(2)	2i	0.7593(9)	1.0507(9)	0.6483(5)	0.039(6)	0.058(7)	0.037(6)	-0.004(5)	0.008(5)	0.018(5)
C(3)	2i	0.744(1)	1.1349(9)	0.7069(5)	0.066(7)	0.052(6)	0.037(6)	0.012(6)	0.017(5)	0.015(5)
C(4)	2i	0.610(1)	1.1365(9)	0.7086(5)	0.046(6)	0.054(6)	0.038(5)	0.012(5)	0.010(5)	0.010(5)
C(5)	2i	0.630(1)	0.8987(9)	0.5406(5)	0.055(6)	0.055(6)	0.036(6)	-0.001(5)	0.010(5)	0.014(5)
C(6)	2i	0.895(1)	1.041(1)	0.6282(6)	0.042(6)	0.057(7)	0.061(7)	0.005(5)	0.020(5)	0.018(6)
C(7)	2i	0.858(1)	1.2178(9)	0.7560(5)	0.066(7)	0.043(6)	0.049(6)	0.003(6)	0.004(6)	0.012(5)
C(8)	2i	0.563(1)	1.2276(9)	0.7581(6)	0.062(7)	0.046(6)	0.062(7)	0.014(6)	0.007(6)	0.012(6)
C(9)	2i	0.536(1)	0.8837(9)	0.8841(5)	0.047(6)	0.045(6)	0.043(6)	0.005(5)	0.016(5)	0.012(5)

Table 3. Continued.

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(10)	2i	0.474(1)	0.7768(9)	0.8409(6)	0.044(6)	0.054(7)	0.049(6)	0.002(5)	0.014(5)	0.016(6)
C(11)	2i	0.375(1)	0.7884(9)	0.7884(5)	0.040(6)	0.053(7)	0.043(6)	-0.004(5)	0.019(5)	0.012(5)
C(12)	2i	0.365(1)	0.9064(9)	0.7943(5)	0.053(6)	0.047(6)	0.043(6)	0.007(5)	0.024(5)	0.012(5)
C(13)	2i	0.640(1)	0.895(1)	0.9472(5)	0.060(7)	0.068(8)	0.047(6)	0.011(6)	0.006(6)	0.021(6)
C(14)	2i	0.496(1)	0.658(1)	0.8501(6)	0.061(7)	0.067(8)	0.065(7)	0.014(6)	0.015(6)	0.021(6)
C(15)	2i	0.284(1)	0.680(1)	0.7380(6)	0.046(6)	0.072(8)	0.064(7)	0.007(6)	0.016(6)	0.010(6)
C(16)	2i	0.256(1)	0.9409(9)	0.7517(6)	0.047(6)	0.052(6)	0.057(7)	0.003(5)	0.003(5)	0.018(5)
C(17)	2i	0.709(1)	0.3369(9)	0.5707(6)	0.038(6)	0.056(7)	0.064(7)	0.004(5)	0.027(5)	0.025(6)
C(18)	2i	0.771(1)	0.2079(9)	0.4807(6)	0.048(6)	0.049(6)	0.056(7)	-0.006(5)	0.008(5)	0.016(6)
C(19)	2i	0.886(1)	0.1849(9)	0.4467(6)	0.057(7)	0.051(6)	0.047(6)	-0.001(6)	0.009(5)	0.012(5)
C(20)	2i	1.046(1)	0.262(1)	0.3733(5)	0.046(6)	0.058(7)	0.044(6)	0.003(5)	0.011(5)	0.004(5)
C(21)	2i	1.098(1)	0.3673(9)	0.3393(5)	0.053(6)	0.061(7)	0.033(5)	0.012(6)	0.008(5)	0.003(5)
C(22)	2i	1.233(1)	0.5654(9)	0.3683(5)	0.064(7)	0.065(7)	0.043(6)	0.022(6)	0.033(5)	0.031(6)
C(23)	2i	1.128(1)	0.358(1)	0.6288(6)	0.058(7)	0.090(9)	0.048(7)	-0.002(7)	0.020(6)	0.015(7)
C(24)	2i	1.223(1)	0.282(2)	0.6326(9)	0.063(9)	0.12(1)	0.11(1)	0.012(9)	0.036(8)	0.05(1)
C(25)	2i	1.350(1)	0.356(1)	0.6116(7)	0.053(7)	0.10(1)	0.077(9)	-0.002(7)	0.014(7)	0.001(8)
C(26)	2i	1.298(1)	0.431(1)	0.5604(7)	0.061(8)	0.10(1)	0.067(8)	-0.007(8)	0.011(7)	0.028(8)
C(27)	2i	1.120(1)	0.7607(9)	0.9157(6)	0.047(6)	0.042(6)	0.070(7)	0.011(5)	0.020(6)	0.021(6)
C(28)	2i	1.285(1)	0.7530(9)	1.0055(6)	0.042(6)	0.046(6)	0.057(6)	0.006(5)	0.012(5)	0.015(5)
C(29)	2i	1.343(1)	0.6676(9)	1.0366(6)	0.044(6)	0.053(6)	0.048(6)	-0.002(5)	0.004(5)	0.003(5)
C(30)	2i	1.300(1)	0.5132(9)	1.1038(5)	0.041(6)	0.051(6)	0.049(6)	0.006(5)	0.005(5)	0.018(5)
C(31)	2i	1.199(1)	0.450(1)	1.1472(6)	0.056(7)	0.053(7)	0.052(6)	0.012(6)	0.012(6)	0.012(5)
C(32)	2i	0.990(1)	0.316(1)	1.1383(6)	0.057(7)	0.058(7)	0.048(6)	0.002(6)	0.010(5)	0.025(6)
C(33)	2i	0.825(1)	0.599(1)	1.1356(6)	0.065(8)	0.066(8)	0.049(7)	-0.005(7)	0.001(6)	0.012(6)
C(34)	2i	0.719(1)	0.664(1)	1.1383(9)	0.067(9)	0.09(1)	0.12(1)	0.011(8)	0.023(9)	0.02(1)
C(35)	2i	0.789(2)	0.781(1)	1.1215(9)	0.12(1)	0.09(1)	0.11(1)	0.07(1)	0.03(1)	0.023(9)
C(36)	2i	0.893(1)	0.755(1)	1.0743(7)	0.065(8)	0.076(9)	0.068(8)	0.010(7)	0.002(7)	0.018(7)
B(1)	2i	0.590(1)	0.7044(9)	0.6611(5)	0.033(6)	0.030(5)	0.038(6)	0.005(5)	0.016(5)	-0.002(5)
B(2)	2i	0.851(1)	0.932(1)	0.8123(6)	0.035(6)	0.044(7)	0.044(6)	0.007(5)	-0.001(5)	0.012(5)

References

- Barbier-Baudry, D.; Blacque, O.; Hafid, A.; Nyassi, A.; Sitzmann, H.; Visseaux, M.: Synthesis and X-ray crystal structures of (C₅H₇Pr) Ln(BH₄)₂(THF) (Ln = Nd and Sm), versatile precursors for polymerization catalysts. *Eur. J. Inorg. Chem.* (2000) 2333-2336.
- Cendrowski-Guillaume, S. M.; Le Gland, G.; Nierlich, M.; Ephritikhine, M.: Lanthanide borohydrides as precursors to organometallic compounds. Mono(cyclooctatetraenyl) neodymium complexes. *Organometallics* **19** (2000) 5654-5660.
- Qian, C.; Nie, W.; Sun, J.: The first example of a dinuclear anionic lanthanoidocene complex: [K(18-crown-6)][(C₁₃H₈)CPh₂(C₅H₄)Nd(BH₄)₂]₂ · C₄H₈O₂. *J. Organomet. Chem.* **626** (2001) 171-175.
- Deng, D.; Zheng, X.; Qian, C.; Sun, J.; Zhang, L.: Studies on organolanthanide complexes XLVII. Syntheses of bis(2-methoxyethylcyclopentadienyl) lanthanide tetrahydroborates (Ln = La, Pr, Nd, Sm or Gd); crystal structures of bis(2-methoxyethylcyclopentadienyl)-praseodymium and neodymium tetrahydroborates. *J. Organomet. Chem.* **466** (1994) 95-100.
- Cendrowski-Guillaume, S. M.; Nierlich, M.; Lance, M.; Ephritikhine, M.: First chemical transformations of lanthanide borohydride compounds: Synthesis and crystal structures of [(η-C₈H₈)Nd(BH₄)(THF)]₂ and [(η-C₈H₈)Nd(THF)₄][BPh₄]. *Organometallics* **17** (1998) 786-788.
- Cendrowski-Guillaume, S. M.; Nierlich, M.; Ephritikhine, M.: Synthesis and X-ray crystal structure of [U(η-C₈H₈)(HMPA)₃][BPh₄], the first cationic monocyclooctatetraenyl compound of uranium(III) and its neodymium homologue. *Eur. J. Inorg. Chem.* (2001) 1495-1498.
- Nief, F.: Complexes containing bonds between group 3, lanthanide or actinide metals and non-first-row main group elements (excluding halogens). *Coord. Chem. Rev.* **178-180** (1998) 13-81.
- Nief, F.; Mathey, F.: A new application of the tetramethylphospholyl (η⁵-C₄Me₄P)π-ligand. Synthesis of η⁵-tetramethylphospholyl complexes of yttrium and lutetium. *J. Chem. Commun., Chem. Soc.* (1989) 800-801.
- Nief, F.; Riant, P.; Ricard, L.; Desmurs, P.; Baudry-Barbier, D.: Synthesis and reactivity of bis(phospholyl)neodymium(III) and -samarium(III) chlorides and alkyl derivatives. *Eur. J. Inorg. Chem.* (1999) 1041-1045.
- Marks, T. J.; Kolb, J. R.: Covalent transition metal, lanthanide and actinide tetrahydroborate complexes. *Chem. Rev.* **77** (1977) 263-293.
- Makhaev, V. D.: Structural and dynamic properties of tetrahydroborate complexes. *Russian Chem. Rev.* **69** (2000) 727-746.
- Sheldrick, G. M.: SHELXTL, version 5.1, Bruker-AXS, Madison, Wisconsin, USA 1999.