

1,1-Diaqua-2,3,4,5,6-pentaisopropoxy-1-nickeladodecaborane

Li-Bin Wu, Jian-Min Dou,*
Qing-Liang Guo, Da-Cheng Li
and Da-Qi WangDepartment of Chemistry, Liaocheng University,
Liaocheng 252059, People's Republic of China

Correspondence e-mail: jmdou@lctu.edu.cn

Key indicators

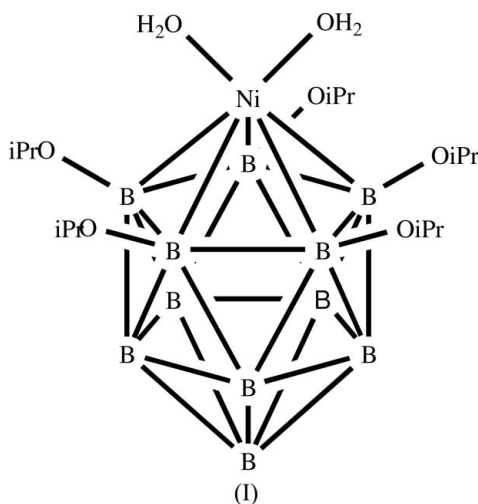
Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.011\text{ \AA}$
 R factor = 0.051
 wR factor = 0.169
Data-to-parameter ratio = 16.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title mononickeladodecaborane cluster, $[\text{NiB}_{11}\text{H}_6(\text{OC}_3\text{H}_7)_5(\text{H}_2\text{O})_2]$, has been synthesized by the reaction of dichlorobis(triphenylphosphine)nickel(II) with triethylammonium *nido*-undecaborane(14) in 2-propanol. The Ni^{IV} atom is connected to five atoms of the boron cage to form a *closo* 12-vertex $\{\text{NiB}_{11}\}$ icosahedral skeleton. All of the H atoms on the five B cage atoms connected to the Ni atom are substituted by isopropoxy groups. The Ni^{IV} atom is also bonded to two water molecules. The molecules form dimers through intermolecular hydrogen-bond interactions.

Received 24 October 2005
Accepted 7 November 2005
Online 16 November 2005

Comment

Boron cluster chemistry has developed into a fruitful area and provided a lot of potentially useful applications, including boron neutron capture therapy (BNCT) of tumours, solvent extraction, materials science, catalysis and host-guest chemistry (Hawthorne, 1993; Hawthorne *et al.*, 1994; Hawthorne & Zheng, 1997; Plesek, 1992; Grimes, 2004). There has been lively theoretical and experimental interest in 12-vertex metallaboranes, and potential starting substrates such as *nido*-undecaborate(14) are easily made from decaborane(14) (Dunks *et al.*, 1981). During research into the coordinating behaviour of *nido*-undecaborate(14) with Ni, the title compound, (I), has been prepared under solvothermal conditions. We present its crystal structure here.



The molecular structure of (I) is shown in Fig. 1. (I) contains one Ni atom and 11 B atoms in a *closo* 12-vertex $\{\text{NiB}_{11}\}$ icosahedral skeleton in which the Ni atom is connected to atoms B2, B3, B4, B5 and B6. The distance of the Ni atom from the B₅ plane is 1.426 (3) Å. All of the five H atoms of this pentagonal B₅ plane were substituted by isopropoxy groups in

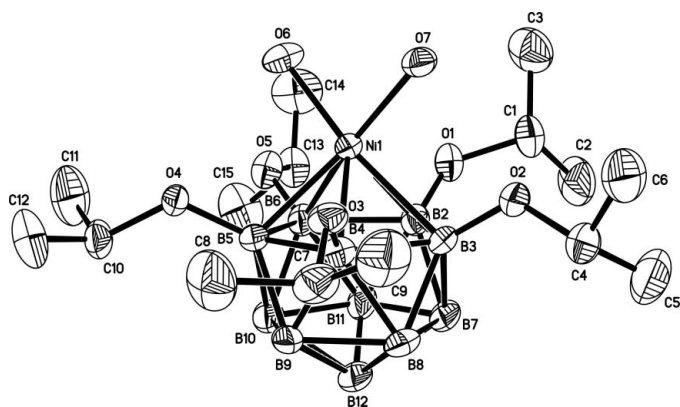


Figure 1
The molecular structure of (1), with the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

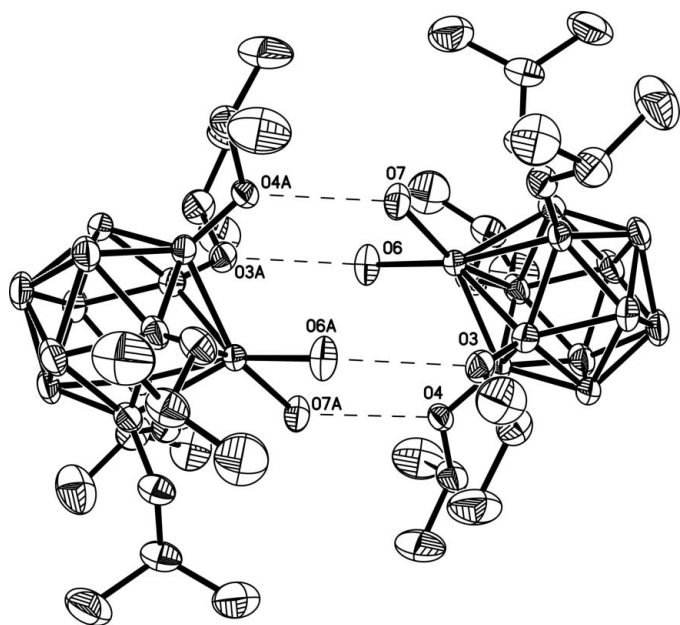


Figure 2
The structure of the hydrogen-bonded (dashed lines) dimer. [Symmetry code: (A) $2 - x, 1 - y, 2 - z$]

the synthesis. The average bond lengths of Ni–B and B–O are 2.123 (7) and 1.393 (9) Å, respectively. The average B–B bond length on the substituted pentagonal face is 1.854 (10) Å, longer than the average length [1.766 (10) Å] of the other B–B bonds in the title cluster. This may be due to the steric effect of the five substituent isopropoxy groups.

Atoms O6 and O7 (water) of one molecule act as donors and atoms O3 and O4 (isopropoxy) of another molecule act as acceptors to form two pairs of O–H...O hydrogen bonds (Table 1). The two molecules are thus linked into a dimer through hydrogen-bond interactions. There is precedent for similar water molecules in other metallaborane clusters, such as [(H₂O)(PPh₃)PdTeB₁₀H₉(PPh₃)]BF₄ (Sheehan *et al.*, 1993). Other examples which take up water during synthetic work-up in air include [(η⁵-C₅Me₅)₃Ir₃B₁₈H₁₅(OH)] (Shea *et al.*, 2000), [7-(η⁵-C₅Me₅)-10-(NEt₃)-*nido*-7,12-RhOB₁₀H₁₀] (Kaur *et al.*,

1996) and [μ-9,9'-O-{5-(η⁵-C₅Me₅)-*nido*-5-RhOB₉H₁₂}]₂] (Ditzel *et al.*, 1990).

Experimental

The synthesis of the title nickelaborane was carried out by reaction of [NiCl₂(PPh₃)₂] (0.260 g, 0.4 mmol) and (Et₃NH)B₁₁H₁₄ (0.188 g, 0.8 mmol) in distilled ¹PrOH in a Teflon-lined autoclave under a dry N₂ atmosphere for 96 h. The solvent was evaporated to dryness under reduced pressure; the residue was dissolved in 5 ml CH₂Cl₂ and chromatographed using dichloromethane/light petroleum (4:1 v/v) as the eluting medium to give a dark-red title compound at R_F = 0.56. The product was recrystallized from *n*-hexane/dichloromethane solution (2:1 v/v); this mixed solvent contained a small amount of water (*ca* 0.3%), from which the aqua ligands of the product are presumably derived. Alternatively, the water could be taken up during the work-up of the product in air, as described in the *Comment*.

Crystal data

[Ni(C₁₅H₄₁B₁₁O₅)(H₂O)₂]
M_r = 515.13
Orthorhombic, *Pbca*
a = 18.656 (2) Å
b = 16.674 (3) Å
c = 18.863 (3) Å
V = 5867.6 (15) Å³
Z = 8
D_x = 1.166 Mg m⁻³

Mo Kα radiation
Cell parameters from 3831 reflections
θ = 2.4–21.8°
μ = 0.69 mm⁻¹
T = 298 (2) K
Block, red
0.45 × 0.38 × 0.29 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.746, T_{max} = 0.825
29382 measured reflections

5173 independent reflections
2618 reflections with I > 2σ(I)
R_{int} = 0.090
θ_{max} = 25.0°
h = -22 → 18
k = -19 → 19
l = -22 → 18

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.051
wR(F²) = 0.169
S = 1.08
5173 reflections
307 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.0565P)² + 10.1219P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.67 e Å⁻³
Δρ_{min} = -0.51 e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
O6–H21...O3 ⁱ	0.80	1.85	2.634 (6)	166
O7–H23...O4 ⁱ	0.81	1.89	2.692 (5)	171

Symmetry code: (i) $-x + 2, -y + 1, -z + 2$.

The isopropoxy and boron cage H atoms were positioned geometrically, with C–H = 0.98 (methine) and 0.96 Å (methyl), and B–H = 1.10 Å, and those on the aqua ligands were found in a difference map. All of the H atoms were treated as riding, with U_{iso}(H) = 1.2U_{eq}(C,B,O).

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics:

SHELXTL (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

The work was funded by the Open Research Fund programme of the Key Laboratory of Marine Drugs (Ocean University of China), the Ministry of Education [KLMD (OCU)2004] and the National Natural Science Foundation of China (No. 20371025).

References

- Bruker (1997). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Ditzel, E. J., Fontaine, X. L. R., Fowkes, H., Greenwood, N. N., Kennedy, J. D., Mackinnon, P., Zhu, S. S. & Thornton-Pett, M. J. (1990). *J. Chem. Soc. Chem. Commun.* pp. 1692–1694.
- Dunks, G. B., Barker, K., Hedaya, E., Hefner, C., Palmer-Ordonez, K. & Remeck, P. (1981). *Inorg. Chem.* **20**, 1692–1697.
- Grimes, R. N. (2004). *J. Chem. Educ.* **81**, 658–672.
- Hawthorne, M. F. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 950–984.
- Hawthorne, M. F., Yang, X. G. & Zheng, Z. P. (1994). *Pure Appl. Chem.* **66**, 245–254.
- Hawthorne, M. F. & Zheng, Z. P. (1997). *Acc. Chem. Res.* **30**, 267–276.
- Kaur, P., Kennedy, J. D., Thornton-Pett, M., Jelinek, T. & Stibr, B. J. (1996). *J. Chem. Soc. Dalton Trans.* pp. 1775–1777.
- Plessek, J. (1992). *Chem. Rev.* **92**, 269–278.
- Shea, S. L., Jelinek, T., Stibr, B., Thornton-Pett, M. & Kennedy, J. D. (2000). *Inorg. Chem. Commun.* **3**, 169–172.
- Sheehan, J. P., Spalding, T. R., Ferguson, G., Gallagher, J. F., Kaitner, B. & Kennedy, J. D. (1993). *J. Chem. Soc. Dalton Trans.* pp. 35–42.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.