Notes

Synthesis, Structural Characterization, and Theoretical Calculations of a New Copper(I)−Octahydrotriborate Complex

C. Serrar, A. Es-sofi, A. Boutalib,* A. Ouassas, and A. Jarid

Département de Chimie, Faculté des Sciences Semlalia,
Université Cadi Ayyad, BP 2390, Marrakech, Morocco

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Introduction

The octahydrotriborate(1−) anion, $[B_3H_8]^-$, is known to act as either a bidentate (η^2) or a tridentate (η^3)[1−14] ligand toward a number of metals. For example, in the $(CO)_3MnB_3H_8$[14] complex, $[B_3H_8]^-$ is a tridentate ligand bound to the manganese atom through three B−H−Mn bridge hydrogen bonds. Its ^{11}B NMR spectrum shows that the three borons have identical environments due to intramolecular exchange between terminal and bridging hydrogens. In contrast, the spectra of complexes in which the triborate ligand coordinates a bidentately exhibit two different boron environments.[9,14] For the $(PPh_3)_2CuB_3H_8$[1−3,7,15] complex, in which $[B_3H_8]^-$ is also bidentate, the ^{11}B NMR spectrum shows one signal. In this note, we report the preparations of the new copper(I) derivatives $[R_4N][ClCuB_3H_8]$ (R = Et, *n*-Pr, *n*-Bu), which are easily isolable. These are the first examples of $LCuB_3H_8$ complexes where L is Cl^-. ^{11}B NMR, ^1H NMR, and IR spectra of this compound are obtained, and theoretical calculations were employed to propose an accurate structure for $[ClCuB_3H_8]^-$.

Experimental and Theoretical Section

All reactions were carried out under an atmosphere of prepurified nitrogen.

Diglyme was distilled over sodium benzophenone, and dichloromethane was dried over CaH_2 and distilled. The $[R_4N][B_3H_8]$ (R = Et, *n*-Pr, *n*-Bu) complexes were prepared by the literature method.[16,17]

^{11}B NMR ($\delta(BF_3\cdot OEt_2) = 0.00$ ppm) and ^1H NMR ($\delta(TMS) = 0.00$ ppm) spectra were recorded at 96.238 MHz (and 128 MHz) and at 300 MHz (and 400 MHz) using a Bruker AM 300 spectrometer (and a Bruker 400 spectrometer). Infrared spectra were obtained for mulls in Nujol on a Perkin-Elmer 683 spectrometer in the range 4000−600 cm^{-1}.

The compounds $[(n\text{-}Bu)_4N][B_3H_8]$ (0.283 g, 1 mmol) and CuCl (0.099 g, 1 mmol) were stirred in dry CH_2Cl_2 (30 mL) for 1 h at 0 °C. No hydrogen evolution was observed during the reaction. The mixture was then filtered, and the filtrate was evaporated to dryness to give a white solid (0.23 g, 61%). At 25 °C, exposure to air, the latter decomposed slowly over a period of days upon to $[BCl_4]^-$ ($\delta(^{11}B) = 1.36$ ppm) and $B(OH)_3$ ($\delta(^{11}B) = 18.8$ ppm). ^{11}B and ^1H NMR (Table 1) and IR (Table 3) spectroscopies and elemental analyses of Cu and Cl (Anal. Calcd for $C_{16}H_{44}NCuCl$: Cu, 16.65; Cl, 9.29. Found: Cu, 16.88; Cl, 9.03) were consistent with the ionic formulation $[(n\text{-}Bu)_4N]^+[ClCuB_3H_8]^-$. Similar results were obtained when the $[Et_4N]^+$ or $[(n\text{-}Pr)_4N]^+$ salt was used instead of the $[(n\text{-}Bu)_4N]^+$ salt.

All calculations were performed using the Gaussian 94[18] system of programs. The basis sets used were 6-31G** for H and B atoms and 3-21G* for Cu and Cl atoms. All geometries were optimized at MP2 and DFT(B3LYP)[19] levels. DFT vibrational frequencies were calculated and compared to those found experimentally. The electronic structures were analyzed by using the natural bond orbital partitioning scheme NBO.[20]

Results and Discussion

Reactions of $[R_4N][B_3H_8]$ (R = Et, *n*-Pr, *n*-Bu) with CuCl in CH_2Cl_2 at 0 °C yielded the new complexes $[R_4N][ClCuB_3H_8]$ as follows:

$$[B_3H_8]^- + CuCl \xrightarrow{CH_2Cl_2} [ClCuB_3H_8]^-$$

The $[ClCuB_3H_8]^-$ formulation is similar to that for $(PPh_3)CuB_3H_8$ given in the literature.[21]

The ^{11}B NMR spectrum of this complex consists of an unresolved multiplet centered at $\delta = -34.5$ ppm in $CDCl_3$ (Table 1) at room temperature. This spectrum is similar to that observed for $(PPh_3)_2CuB_3H_8$ (broad signal centered at $\delta = -32.5$ ppm),[7] in which the octahydrotriborate ligand is bidentate (η^2), but is markedly different from those of CuB_3H_8[21] and the $[B_3H_8]^-$ anion.[22] On ^1H decoupling, a single very narrow

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(1) Lippard, S. J.; Ucko, D. A. *Chem. Commun.* **1967**, 983.
(2) Lippard, S. J.; Ucko, D. A. *Inorg. Chem.* **1968**, 7, 1051.
(3) Lippard, S. J.; Melmed, K. M. *Inorg. Chem.* **1969**, *8*, 2755.
(4) Muetterties, E. L.; Peet, W. G.; Wegner, P. A.; Alegranti, C. W. *Inorg. Chem.* **1970**, *9*, 2474.
(5) Borlin, J.; Gaines, D. F. *J. Am. Chem. Soc.* **1972**, *94*, 1367.
(6) Calabress, J. C.; Gaines, D. F.; Hildebrandt, S. J.; Morris, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 5489.
(7) Klamberg, F.; Muetterties, E. L.; Guggenberger, L. J. *Inorg. Chem.* **1968**, *7*, 7272.
(8) Bown, M.; Fontaine, X. L. R.; Greenwood, N. N.; Mackinnon, P.; Kennedy, J. D.; Pett, M. J. *J. Chem. Soc., Dalton Trans.* **1987**, 2781.
(9) Pulham, C. R.; Downs, A. J.; Rankin, H.; Robertson, H. E. *J. Chem. Soc., Chem. Commun.* **1990**, 1520.
(10) Burns, I. D.; Hill, A. F.; Thompsett, A. R. *J. Organomet. Chem.* **1992**, *C8*, 425.
(11) Alcock, N. M.; Burns, I. D.; Claire, K. S.; Hill, A. F. *Inorg. Chem.* **1992**, *31*, 2906.
(12) Burns, I. D.; Hill, A. F.; Williams, D. J. *Inorg. Chem.* **1996**, *35*, 2685.
(13) Hildebrandt, S. J.; Gaines, D. F. *J. Am. Chem. Soc.* **1974**, *96*, 5574.
(14) Hildebrandt, S. J.; Gaines, D. F.; Calabress, J. C. *Inorg. Chem.* **1978**, *17*, 790.
(15) Beckett, M. A.; Jones, P. W. *Synth. React. Inorg. Met.-Org. Chem.* **1997**, *27*, 41.
(16) Dewkett, W. J.; Grace, M.; Beall, H. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1279.
(17) Dunks, G. B.; Ordonnez, K. P. *Inorg. Chem.* **1978**, *17*, 1514.
(18) Frisch, J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision B.1; Gaussian, Inc.: Pittsburgh, PA, 1995.
(19) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(20) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(21) Hertz, R. K.; Goetze, R.; Shore, S. G. *Inorg. Chem.* **1979**, *18*, 2813.
(22) Hill, T. G.; Godfroid, R. A.; White, J. P., III; Shore, S. J. *Inorg. Chem.* **1991**, *30*, 2952.

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Table 1. $^1H\{^{11}B\}$ and ^{11}B NMR Data for the $[Bu_4N][ClCuB_3H_8]$ Complex

δ, ppm CDCl$_3$	δ, ppm CD$_2$Cl$_2$	rel intens	assgnt
^{11}B ($\delta(BF_3{\cdot}OEt_2) = 0.00$ ppm)			
−34.5 (m)	−36.0	3B	B(**1**−**3**)
−34.8 (m)[a]			
−37.0 (m)[b]			
^1H (δ(TMS) = 0.00 ppm)			
0.98 (m)	0.96 (m)	12H	CH_3
1.39 (q)	1.41 (q)	8H	CH_2
1.65 (m)	1.82 (m)	8H	CH_2
3.2 (m)	3.15 (m)	8H	CH_2
0.02 (m)	0.08 (m)	8H	BH
−0.25 (m)[a]			
−1.5 (m)[b]			

[a] At −30 °C. [b] At −50 °C.

resonance is observed, indicating equivalence of the three boron environments. The fine structure disappears as the temperature is lowered, but the spectrum remains essentially unchanged down to −50 °C, indicating that the fluxional behavior of this complex is still rapid at this temperature. The ^{11}B NMR spectrum of the $[ClCuB_3H_8]^-$ anion was also very similar to that observed for the $(CO)_3MnB_3H_8$[14] complex, in which $[B_3H_8]^-$ acts as a tridentate ligand toward the manganese atom. The room-temperature ^1H NMR (^{11}B decoupled) spectrum of this complex consists of a broad signal of area 8 at 0.02 ppm (vs Me_4Si in $CDCl_3$) which is assigned to the hydrogens on boron. This signal, which is similar to those observed for the $(PPh_3)CuB_3H_8$[21] complex and the free $[B_3H_8]^-$ anion,[22] remains almost the same at −50 °C. These results show that the equivalence of the three boron atoms in this complex is due to a rapid intramolecular exchange between the hydrogen atoms (on the NMR time scale) analogous to that found in the $[B_3H_8]^-$ anion and in several complexes containing hydroborate ligands. Even at low temperatures (below −50 °C), this process is rapid.

The infrared spectrum of $[Bu_4N][ClCuB_3H_8]^-$ (Table 3) exhibits strong terminal B−H stretching absorptions at 2480 and 2420 cm^{-1} and three weak bands at 2120, 2050, and 2000 cm^{-1} due to bridging B−H−B and B−H−Cu vibrations. This spectrum is comparable to the spectra of $(PPh_3)_2CuB_3H_8$,[7] CuB_3H_8,[21] and other $M{-}B_3H_8$ complexes.[14] It indicates the presence of two types of hydrogen (bridging and terminal) in the static structure of $[ClCuB_3H_8]^-$. Furthermore, several bands observed in 750−1480 and 2860−2970 cm^{-1} regions are consistent with the presence of the $(n\text{-}Bu)_4N^+$ group.

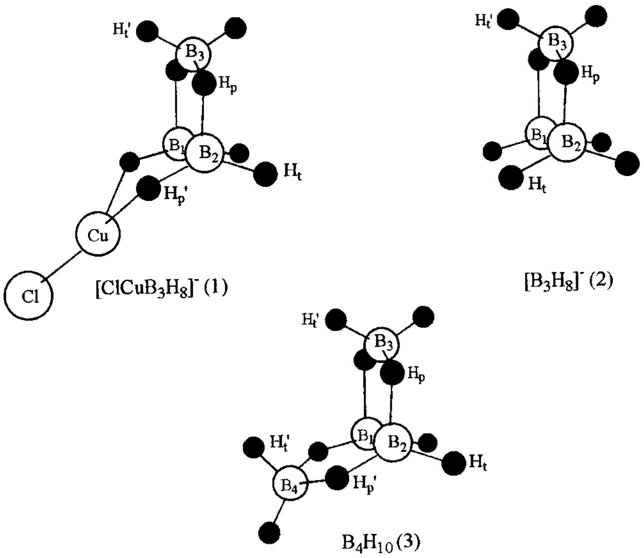

Figure 1. Optimized structures **1**−**3**.

Table 2. Selected Interatomic Distances (Å) for $[ClCuB_3H_8]^-$ (**1**), $[B_3H_8]^-$ (**2**), and B_4H_{10} (**3**)

	$[ClCuB_3H_8]^-$ MP2	$[ClCuB_3H_8]^-$ DFT	$[B_3H_8]^-$ MP2	$[B_3H_8]^-$ DFT	$[B_3H_8]^-$ expt[a]	B_4H_{10} MP2	B_4H_{10} DFT	B_4H_{10} expt[b]
B_1B_2	1.798	1.809	1.824	1.846	1.80	1.720	1.722	1.75
B_1B_3	1.802	1.816	1.783	1.792	1.77	1.842	1.862	1.845
B_1H_p	1.249	1.257	1.257	1.262	1.20	1.246	1.257	1.21
B_3H_p	1.436	1.447	1.465	1.494	1.50	1.408	1.413	1.37
B_1H_t	1.192	1.199	1.203	1.210	1.05−1.2	1.178	1.184	1.05−1.17
B_3H_t'	1.198	1.203	1.205	1.211	1.05−1.2	1.190	1.195	1.05−1.17
B_1H_p'	1.246	1.252				1.246	1.257	1.21
$H_p'Cu$	1.742	1.764						
$H_p'B_4$						1.408	1.413	1.37
B_1Cu	2.199	2.227						
B_1B_4						1.842	1.862	1.840
CuCl	2.188	2.203						
	2.118[c]	2.109[c]						

[a] Reference 24. [b] Reference 23. [c] Calculated distance of free CuCl.

Table 3. DFT Vibrational Frequencies for $[ClCuB_3H_8]^-$ and$[B_3H_8]^-$ Compared to Experimental Frequencies for $[(n\text{-}Bu)_4N][ClCuB_3H_8]$, $[(n\text{-}Bu)_4N][B_3H_8]$, and $(PPh_3)_2CuB_3H_8$

ν_{calcd},[a] cm^{-1} $[ClCuB_3H_8]^-$	ν_{calcd},[a] cm^{-1} $[B_3H_8]^-$	ν_{exptl}, cm^{-1} $[(n\text{-}Bu)_4N]$-$[ClCuB_3H_8]$[b]	ν_{exptl}, cm^{-1} $[(n\text{-}Bu)_4N]$-$[B_3H_8]$[b]	ν_{exptl}, cm^{-1} $(PPh_3)_2$-CuB_3H_8[c]
2595 (348)	2529 (690)	2480 (100)	2450 (100)	2489
2583 (14)	2508 (3)	2420 (99)	2400 (94)	2400
2576 (58)	2504 (0)	2380 (82)	2340 (30)	
2530 (169)	2493 (1)	2300 (30)	2300 (25)	
2263 (136)	2462 (415)	2120 (63)	2130 (23)	2125
2243 (5)	2242 (172)	2050 (46)	2080 (19)	2100
2184 (35)	2194 (46)	2000 (49)		
2161 (168)				

[a] Calculated intensities are given in parentheses. [b] Relative intensities of the experimental bands are given in parentheses. [c] Reference 7.

We performed calculations using MP2 and DFT levels of theory to complete the experimental observations and propose a correct structure for $[ClCuB_3H_8]^-$. The $[B_3H_8]^-$, B_4H_{10}, and $[ClCuB_3H_8]^-$ structures used in this study are reported in Figure 1. Their MP2 and DFT optimized geometrical parameters are listed in Table 2. In Table 3, we give DFT unscaled vibrational frequencies in 2000−2600 cm^{-1} range which are compared to those experimentally observed. The MP2 and DFT geometrical parameters for the $[B_3H_8]^-$ (**2**) and B_4H_{10} (**3**) structures are in good agreement with X-ray[23,24] data (Table 2) and other accurate calculations.[25,26] For $[B_3H_8]^-$ (**2**) and B_4H_{10} (**3**), the largest deviations are 0.03 and 0.05 Å for B−B distances and 0.06 and 0.07 Å for B−H distances at the MP2 and DFT levels, respectively. In the $[ClCuB_3H_8]^-$ case, both MP2 and DFT optimizations led to structure **1** (Figure 1), which is the most stable. In this structure, the $[B_3H_8]^-$ ligand is bound to Cu through two bridging hydrogens. In contrast, the η^3-coordination (similar to that for $(CO)_3MnB_3H_8$) optimization in total potential surface leads to the η^2 structure **1**. This shows the instability of η^3 coordination of $[B_3H_8]^-$ around Cu in this complex. The MP2 and DFT values for the unbridged B_1B_2 bond length (1.798 and 1.809 Å, respectively) are slightly less than those for the bridging B_1B_3 bond length (1.802 and 1.816 Å, respectively). These

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(23) Nordman, C. E.; Lipscomb, W. N. *J. Chem. Phys.* **1953**, *21*, 1856.
(24) Peters, C. R.; Nordman, C. E. *J. Am. Chem. Soc.* **1960**, *82*, 5758.
(25) Serrar, C.; Es-sofi, A.; Boutalib, A.; Ouassas, A.; Jarid, A. *J. Mol. Struct. (THEOCHEM)* **1999**, *491*, 161.
(26) Bühl, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 477.

values are analogous to those found in B_4H_{10} (**3**) (Table 2). In contrast, the scenario is reversed in the $[B_3H_8]^-$ case of **2** (B_1B_2 = 1.824 and 1.846 Å and B_1B_3 = 1.783 and 1.792 Å, respectively, at the MP2 and DFT levels). This is in agreement with the fact that structure **1** is derived from *arachno*-decahydrotetraborane, B_4H_{10}, in which the $[BH_2]^+$ group is replaced by a CuCl fragment. We also note that the Cu atom is not situated in the same plane as that of B_1, B_2, and bridging hydrogens ($B-H_p{}'-Cu$). The calculated dihedral angle between the Cu atom and the $B_1B_2H_p{}'$ plane is about 41° at both the MP2 and DFT levels. This atomic disposition is probably due to the slight interaction between the Cu atom and the two boron atoms of the unbridged bond. This is confirmed by the NBO calculated charges, which indicate a slight variation of B_1 and B_2 atom charges on going from free $[B_3H_8]^-$ to $[CuClB_3H_8]^-$ (**1**) (−0.39 to −0.48 and −0.45 to −0.54 at the MP2 and DFT levels, respectively). These results may explain the stability of the coordination mode around the Cu metal in this complex. Otherwise, the stability of **1** may be explained by the fact that, in free $[B_3H_8]^-$ (**2**), the B_1 and B_2 atoms are rich in electrons compared to the B_3 atom (−0.15 and −0.26 at the MP2 and DFT levels, respectively). Therefore, the attack of the Cu center on the unbridged B_1B_2 bond is most favorable.

DFT vibrational frequencies show that structures **1**−**3** for $[ClCuB_3H_8]^-$, $[B_3H_8]^-$, and B_4H_{10} are true minima. The unscaled vibrational frequencies of $[ClCuB_3H_8]^-$, in the range 2000−2600 cm^{-1} (Table 3), are in agreement with those obtained experimentally. These calculated frequencies are also in good agreement with those observed for the $(PPh_3)_2CuB_3H_8$ complex.

Our theoretical study also predicted a high absolute values for the $[ClCuB_3H_8]^-$ complexation energy (−70.3 and −69.82 kcal mol^{-1} at the MP2 and DFT levels, respectively). These values indicate that the Cu atom is strongly bound to the $[B_3H_8]^-$ ligand. This is also shown by the Cu−Hp′ bond lengths (1.742 and 1.764 Å at the MP2 and DFT levels, respectively). These data thus support the above results and the proposed structure **1** for this complex.

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