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THE STRUCTURE OF BIGUANIDE COMPLEXES OF BORON

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Abstract—Biguanide complexes of boron have been investigated as potential exterior grade fixed boron wood preservatives. Two biguanide rings are necessary for achieving moderate hydrolytic stability in application to wood. The complexes $B(big)(OH)_2$ (**1**) and $B(big)_2Cl$ (**2**) (big = biguanide) have been investigated by ^{11}B and ^{13}C NMR spectroscopy and their structures determined by X-ray crystallography.

Various boron compounds are used as wood preservatives, but their usage is restricted to interior applications.[1] The extension of the use of boron as an exterior grade preservative is attractive in view of its much lower mammalian and environmental toxicity than the commonly used copper–chromium–arsenic preservatives.[2] Accordingly biguanide complexes of boron have been investigated for their potential as fixed boron soft-wood preservatives.

EXPERIMENTAL

NMR spectra were acquired using a Bruker AC-200 spectrometer. ^{11}B spectra were recorded in H_2O solution using a broadband probe and sodium borohydride reference. Biguanidine[3] and *tris* (dimethylamino)borane[4] were prepared by standard methods.

B(biguanide)$(OH)_2 \cdot H_2O$ (1)

A solution of 3.66 g of boric acid (0.059 mol) in 7.0 cm^3 water at 80°C was added to a solution of 6.0 g of biguanidine (0.059 mol) in 12 cm^3 water at 80°C. On cooling to 20°C the product separated as a white precipitate. This was recrystallised from hot water to give the pure product as white crystals, yield 7.2 g (75%).

B(biguanide)$_2Cl \cdot 0.5H_2O$ (2)

This was prepared according to a literature method.[5] A solution of 18.45 cm^3 *tris* (dimethylamino)borane (0.099 mol) in 25 cm^3 dry pyridine was added dropwise to a stirred solution of 20 g biguanidine in 400 cm^3 of hot pyridine. An insoluble precipitate formed. After refluxing for 2 h the precipitate was filtered and washed with toluene. The product was suspended in water (25 cm^3), and heated to dissolve. The pH of the solution was adjusted to 5 with 1 mol l^{-1} HCl, and the solution concentrated on a rotary evaporator. This was recrystallised from hot water to give fine needles of **2**, yield 7.3 g (33%).

Crystal structure determination

Crystals were mounted on silica fibres on a Nonius CAD-4 diffractometer for data collection. Cell par-

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ameters were obtained by a least-squares fit to the four circle coordinates of 25 reflections. Data were corrected for Lorentz and polarisation effects but no absorption correction was considered necessary. A summary of the X-ray data is given in Table 1.

The structures were solved by direct methods[6] and refined by full-matrix least-squares.[7] All non-hydrogen atoms were allowed to assume anisotropic thermal parameters. Hydrogen atoms were located from electron density maps and allowed to refine isotropically. Final electron density maps showed peak maxima of 0.5 e Å^{-3}, randomly distributed. Final refinement data are given in Table 1. Material deposited comprises atomic coordinates, thermal parameters, bond angles and observed and calculated structure factors.

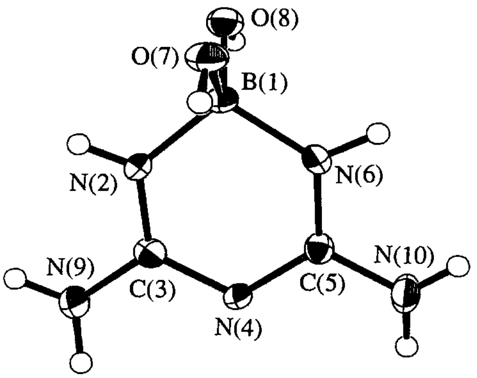

Fig. 1. The molecular structure of B(biguanide)(OH)$_2$·H$_2$O (**1**).

RESULTS AND DISCUSSION

The structures of $C_2H_8BN_5O_2 \cdot H_2O$ (**1**) and $[C_4H_{12}BN_{10}]Cl \cdot 0.5H_2O$ (**2**) are illustrated in Figs 1 and 2 respectively which also give the molecular numbering. Interatomic distances and angles are given in Tables 2 and 3. The structures comprise unique molecules or cations which are linked together by hydrogen bonding involving both the water molecules and direct links between molecules. Hydrogen bond interactions are tabulated in Table

Table 1. Crystal data for **1** and **2**

	1	**2**
Formula	$C_2H_{10}BN_5O_3$	$C_4H_{13}BClN_{10}O_{0.5}$
Molecular weight	162.96	255.5
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	*Pbcn*
a (Å)	6.871(2)	9.363(3)
b (Å)	9.766(1)	15.025(1)
c (Å)	10.843(2)	15.247(1)
V (Å^3)	727.6(4)	2144.9(9)
Z	4	8
d (calc) (g cm^{-3})	1.501	1.582
F(000)	344	1064
μ (cm^{-1})	0.9	3.0
Radiation Mo-K_α (Monochromatic) λ (Å)	0.71069	0.71069
Temperature (K)	293	293
Diffractometer	Nonius CAD-4	Nonius CAD-4
Scan technique	$\omega/2\theta$	$\omega/2\theta$
2θ (min – max) (°)	2–60	3–50
No. of reflections	1114	1880
No. of observed reflections $I > 2\sigma(I)$	575	1572
Crystal size (mm)	0.18 × 0.26 × 0.38	0.22 × 0.28 × 0.45
Least-squares weights g	0.001	0.53
No. of variables in LS	141	202
Goodness of fit on F^2	0.527	1.053
Function minimised	$\Sigma w(F_o^2 - F_c^2)^2$	
R and $wR2$	0.029 0.055	0.030 0.079
Peak height in final density map (min – max) (e A^{-3})	0.15–0.13	0.17–0.23
Least-squares weights	$1.0/[\sigma^2(F_o^2) + \{g(F_o^2 + 2F_c^2)/3\}^2]$	

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

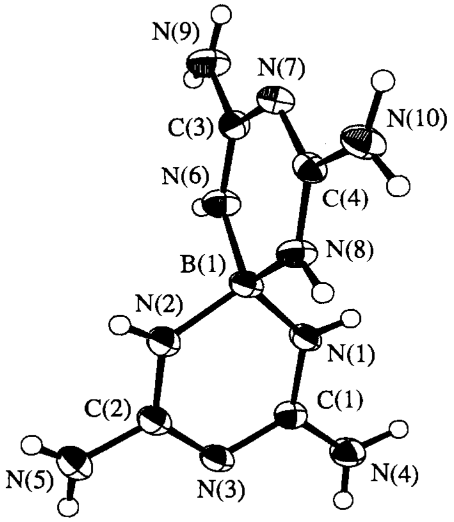

Fig. 2. The molecular structure of B(biguanide)$_2$ Cl$\cdot$0.5H$_2$O (**2**).

4. The rings are highly symmetrical indicative of electron delocalisation around the rings. The average B—N distance in **1** is longer than that in **2**, 1.541 against 1.525 Å, due to bonding to the more electronegative oxygen in **1**.

Table 2. Bond lengths (Å) and angles (°) for **1**

B(1)—O(7)	1.452(4)
B(1)—O(8)	1.466(4)
B(1)—N(2)	1.539(4)
B(1)—N(6)	1.543(4)
N(2)—C(3)	1.322(3)
C(3)—N(4)	1.343(3)
C(3)—N(9)	1.348(3)
N(4)—C(5)	1.351(3)
C(5)—N(6)	1.327(3)
C(5)—N(10)	1.339(4)
O(7)—B(1)—O(8)	105.2(2)
O(7)—B(1)—N(2)	113.1(3)
O(8)—B(1)—N(2)	111.1(3)
O(7)—B(1)—N(6)	111.5(3)
O(8)—B(1)—N(6)	112.6(3)
N(2)—B(1)—N(6)	103.6(2)
C(3)—N(2)—B(1)	125.5(2)
N(2)—C(3)—N(4)	124.1(2)
N(2)—C(3)—N(9)	120.0(2)
N(4)—C(3)—N(9)	115.9(2)
C(3)—N(4)—C(5)	117.7(2)
N(6)—C(5)—N(10)	120.2(2)
N(6)—C(5)—N(4)	123.3(2)
N(10)—C(5)—N(4)	116.6(2)
C(5)—N(6)—B(1)	125.7(2)

Table 3. Bond lengths (Å) and angles (°) for **2**

B(1)—N(3)	1.519(2)
B(1)—N(1)	1.521(2)
B(1)—N(6)	1.529(2)
B(1)—N(8)	1.531(2)
N(1)—C(1)	1.321(2)
N(2)—C(2)	1.343(2)
N(2)—C(1)	1.351(2)
N(3)—C(2)	1.330(2)
N(4)—C(1)	1.337(2)
N(5)—C(2)	1.339(2)
N(6)—C(3)	1.323(2)
N(7)—C(3)	1.348(2)
N(7)—C(4)	1.350(2)
N(8)—C(4)	1.328(2)
N(9)—C(3)	1.337(2)
N(10)—C(4)	1.340(2)
N(3)—B(1)—N(1)	104.50(14)
N(3)—B(1)—N(6)	111.9(2)
N(1)—B(1)—N(6)	112.53(14)
N(3)—B(1)—N(8)	113.12(14)
N(1)—B(1)—N(8)	111.09(14)
N(6)—B(1)—N(8)	103.90(13)
C(1)—N(1)—B(1)	125.6(2)
C(2)—N(2)—C(1)	116.84(14)
C(2)—N(3)—B(1)	125.0(2)
C(3)—N(6)—B(1)	125.8(2)
C(3)—N(7)—C(4)	117.13(14)
C(4)—N(8)—B(1)	125.58(14)
N(1)—C(1)—N(4)	120.2(2)
N(1)—C(1)—N(2)	123.5(2)
N(4)—C(1)—N(2)	116.3(2)
N(3)—C(2)—N(5)	119.0(2)
N(3)—C(2)—N(2)	124.2(2)
N(5)—C(2)—N(2)	116.8(2)
N(6)—C(3)—N(9)	119.2(2)
N(6)—C(3)—N(7)	123.8(2)
N(9)—C(3)—N(7)	117.0(2)
N(8)—C(4)—N(10)	120.0(2)
N(8)—C(4)—N(7)	123.7(2)
N(10)—C(4)—N(7)	116.3(2)

The molecular packing in **1** is shown in Fig. 3. The water molecule makes close approaches to the hydroxyl oxygens of two borate molecules through its hydrogen atoms and additional approaches to two hydrogens linked to nitrogen atoms. There are additional interactions between the hydroxyl oxygen atoms and amine hydrogens on adjacent molecules. The result of all of these interactions is to place all oxygen atoms in a tetrahedral environment.

The molecular packing in **2** is shown in Fig. 4. The chloride ion makes eight close approaches to amine hydrogen atoms suggestive of hydrogen bonds (Table 4). The water molecule makes hydrogen bond approaches to an amine hydrogen through its oxygen atom and an imine nitrogen

Table 4. Hydrogen bond interactions (Å)

1		**2**	
Atom···Atom	Sym	Atom···Atom	Sym
H(9)···O(1)	2.10 2	H(5)···Cl	2.58
H(2)···O(1)	2.17 3	H(3)···Cl	2.59
O(7)···H(1)	1.92 2	H(9)···Cl	2.76 2
O(8)···H(1)	1.91 4	H(5)···Cl	3.00 3
		H(6)···Cl	2.94 4
H(9)···O(7)	2.07 4	H(9)···Cl	2.42 4
H(10)···O(8)	2.08 2	H(4)···Cl	2.53 5
		H(10)···Cl	2.77 5
		H(4)···O(1)	2.25 6
		N(7)···H(7)	2.32 3
Symmetry transformations			
2 $1/2-x, -y, 1/2+z$		2 $1/2-x, 1/2-y, 1/2+z$	
3 $1/2+x, 1/2-y, -z$		3 $1/2+x, 1/2-y, -z$	
4 $-x, 1/2+y, 1/2-z$		4 $-x, y, 1/2-z$	
		5 $x, -y, 1/2+z$	
		6 $1/2+x, 1/2+y, 1/2-z$	

through its hydrogen atom, completing the tetrahedral environment around this molecule. The borate cations are linked together through these hydrogen bond networks, and there are no direct links between cations as found in **1**.

At high pH **1** shows a single signal at -1.65 ppm in the ^{11}B NMR spectrum indicative of a tetrahedral boron atom. At pH 7 the ^{11}B spectrum of **1** showed a second signal at 18.65 ppm due to $B(OH)_3$. Compound **1**, therefore, did not show the required stability for application to wood. In contrast, **2** showed a signal at -4.09 ppm in the ^{11}B spectrum which did not change, even in water at pH 3. These NMR data show that two biguanide chelate rings attached to boron are necessary to provide stability in the wood matrix.

The crystal structures show that hydrogen bonding is extensive in the solid state. Both cellulose and lignin provide many possible sites for hydrogen bonding of **2** within the wood structure. Results from the treatment of wood with both **1** and **2** and biological testing of the products will be reported elsewhere.

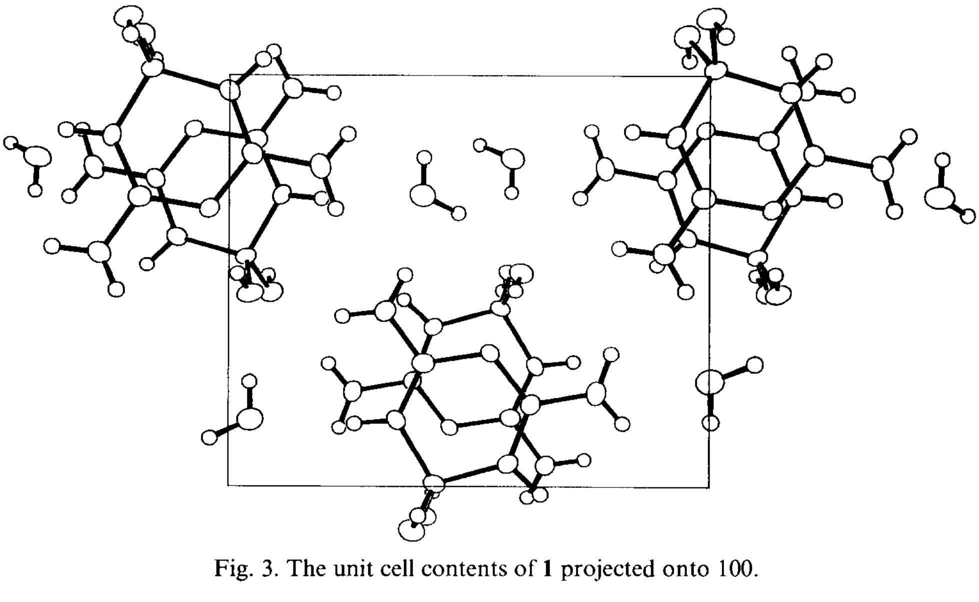

Fig. 3. The unit cell contents of **1** projected onto 100.

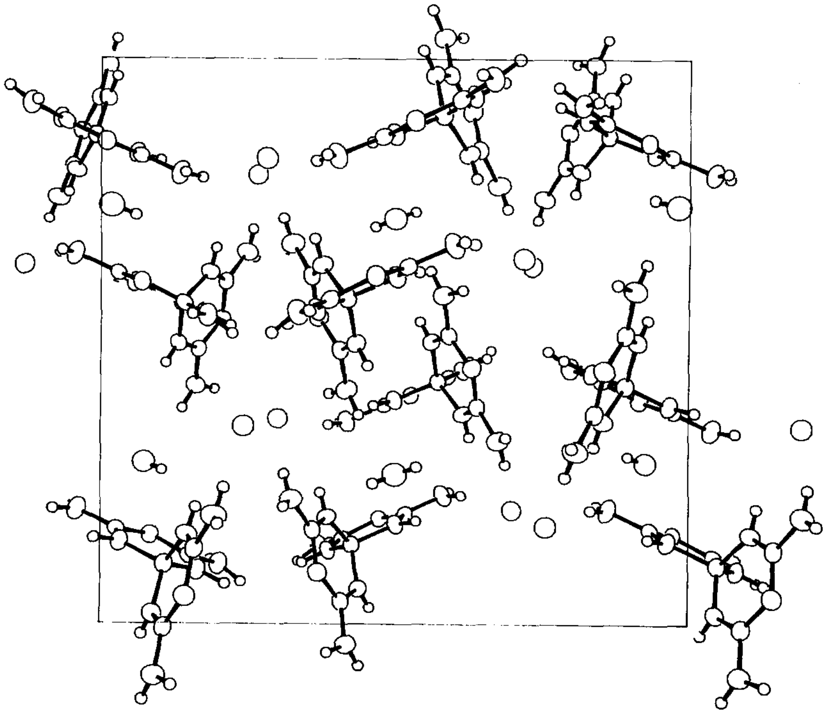

Fig. 4. The unit cell contents of **2** projected onto 010.

REFERENCES

1. R. Cockroft and J. F. Leavy, *J. Inst. Wood Science* 1973, **6**, 28.
2. *Wood Preservation with Boron*. New Zealand Wood Preservation Association Inc., Information Bulletin 2.
3. S. N. Holter and W. C. Fernelius, *Inorg. Synth.* 1963, **7**, 58.
4. K. Niedensu and J. W. Dawson, *Inorg. Synth.* 1967, **10**, 135.
5. J. E. Milks, G. W. Kennerly and J. H. Pollevy, *J. Am. Chem. Soc.* 1962, **84**, 2529.
6. G. N. Sheldrick, SHELXS-86, Institut für Anorganische Chemie, Universität Göttingen, Germany (1986).
7. G. N. Sheldrick, SHELXL-93, Institut für Anorganische Chemie, Universität Göttingen, Germany (1993).