

Table 6. *Hydrogen-bonding geometry* (Å, °) for (2)

D—H...A	D—H	H...A	D...A	D—H...A
N16—H161...O1W <sup>1</sup>	0.86 (5)	1.96 (5)	2.784 (6)	162 (4)
O1W—H1W...O13 <sup>ii</sup>	0.87 (7)	2.06 (7)	2.923 (7)	171 (6)
O1W—H1W...O2	0.93 (8)	1.78 (8)	2.680 (7)	161 (6)

Symmetry codes: (i) 2 - x, ½ + y, 1 - z; (ii) 1 + x, y - 1, z.

The rather poor crystal quality caused high e.s.d.'s in all parameters; reflections with net negative measured intensities were suppressed in the refinement. H atoms were refined with a riding model and with *U*<sub>iso</sub>(H) set at 1.2 (1.5 for methyl groups) times *U*<sub>eq</sub> of the bonded atom; the positions of the N—H and H<sub>2</sub>O H atoms were freely refined.

For both compounds, data collection: *KM-4 Software* (Kuma Diffraction, 1992); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *Stereochemical Workstation* (Siemens, 1989); software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## A Triphenylboroxin Derivative Possessing Two Intramolecular Chelates

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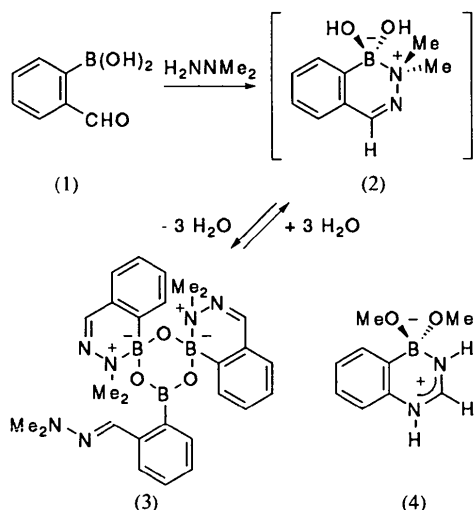
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### Abstract

Condensation of 2-formylbenzeneboronic acid and 1,1-dimethylhydrazine afforded the title compound, bis-(8-*B*-4)-1,3,5-tris{2-[(*N,N*-dimethylhydrazono)methyl]-phenyl}boroxin, C<sub>27</sub>H<sub>33</sub>B<sub>3</sub>N<sub>6</sub>O<sub>3</sub>, a tridehydro cyclic trimer of the expected simple benzaldehyde hydrazone and the first triphenylboroxin derivative found to possess two B chelating interactions. The double chelation induces molecular asymmetry but effects only a slight puckering in the central boroxin ring.

### Comment

In an investigation parallel to that of our study of the physicochemical properties of 2,4,1-benzoxaza- and benzodiazaborines, we are undertaking a similar examination of their 2,3,1-isomeric counterparts in order to delineate the similarities and differences between these two classes of structurally related heterocycles. It has been known for quite some time that the condensation of 2-formylbenzeneboronic acid (1) with hydroxylamine and hydrazine-based carbonyl derivatizing reagents can be used to prepare bicyclic 2,3,1-benzoxaza- and benzodiazaborines, respectively (Tschampel & Snyder, 1964; Dewar & Dougherty, 1964). One potential member of this latter class of heterocycles is the previously unknown *N,N*-dimethylhydrazone, (2), a compound we view with some interest because in an internally chelated, zwitterionic structural form it would bear some resemblance to (4), a bis-methanol adduct of 1,2-dihydro-1-hydroxy-2,4,1-benzodiazaborine we examined recently by X-ray crystallographic and other means (Groziak, Ganguly & Robinson, 1994). We now relate that (2) obtained *via* the condensation of (1) and 1,1-dimethylhydrazine exists in tridehydro trimeric form as the substituted triphenylboroxin (3) in the solid state. Compound (2) can be obtained *via* gentle hydrolysis of (3) effected by simple dissolution in water at 298 K, but it deboronates in this medium at temperatures near 373 K. Evaporation of an aqueous solution of (2) results in the regeneration of (3).



An ORTEP (Johnson, 1965) view of the molecule of crystalline (3), together with its atom numbering, is provided in Fig. 1. The molecular structure of (3) has many features of interest and is apparently unique as the first crystalline triphenylboroxin derivative to exhibit two  $\text{B}_3\text{O}_3$  ring chelation events. These occur on opposite faces of the ring, and arise from the intramolecular interaction of a B center with a terminal N atom of a 2-(*Z*)-(1,1-dimethylhydrazono)methyl moiety substituent on a phenyl ring. The sole dimethylhydrazone moiety that is not involved in such a chelation, perhaps because of steric congestion at either face of the already doubly chelated  $\text{B}_3\text{O}_3$  ring, exists in *E*-rotational isomeric form, again as a likely consequence of steric congestion. The barrier for interconversion of *syn* and *anti* rotamers in hydrazones is known to be low. The chirality induced by double intramolecular chelation in (3) explains its racemic nature.

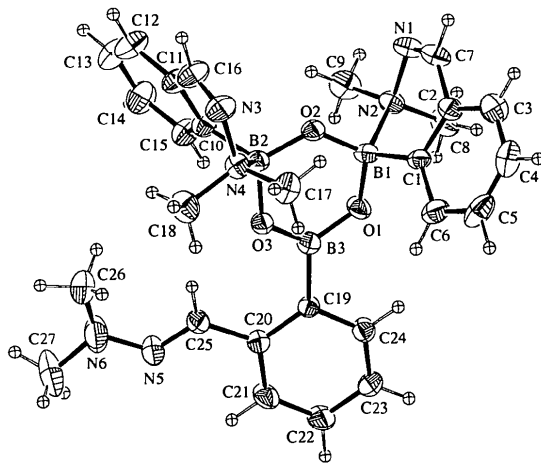


Fig. 1. Molecular configuration and atom-numbering scheme for compound (3) with displacement ellipsoids at the 30% probability level. H atoms are shown as isotropic spheres of arbitrary radii.

Several 1,3,5-triphenylboroxins have been examined by crystallographic methods to date, and some have been the subject of a recent MNDO structural study (Sporzyński & Szatylowicz, 1994). The parent compound 1,3,5-triphenylboroxin (Brock, Minton & Niedenzu, 1987) is devoid of any significant chelation opportunities and has been found to have a nearly planar  $\text{B}_3\text{O}_3$  central ring with nearly coplanar phenyl rings as substituents. In a 2:1 complex with 1,4-benzenediamine (Yalpani & Boese, 1983) or in a 1:1 complex with 2,4-pentanedione (Köster, Angermund, Sporzyński & Serwatowski, 1986), however, one of the  $\text{B}_3\text{O}_3$  ring B centers undergoes intermolecular chelation, and the central ring then exhibits a non-planar topography. Even though it is doubly chelated, the central  $\text{B}_3\text{O}_3$  ring in (3) exists in only a slightly puckered [0.078(4) Å mean deviation from plane] distorted boat conformation as shown in Fig. 2 which displays orthogonal edge-on views of this ring. The two N—B chelation events have occurred on opposite faces of the  $\text{B}_3\text{O}_3$  ring, presumably in avoidance of steric interaction between dimethylamino moieties. A few of the more interesting features of this ring include significantly short B3—O bond lengths (Table 2) at the unchelated  $sp^2$ -hybridized B center indicative of significant *p* electron donation from O1 and O3, and wider internal ring angles at the O2 and B3 centers (Ta-

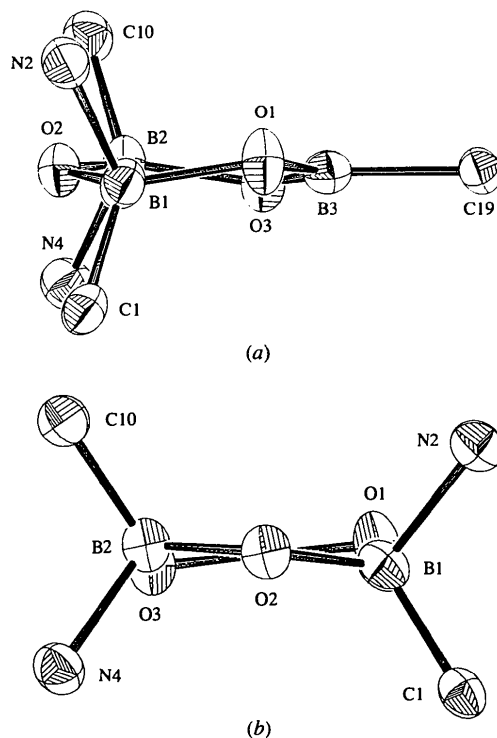


Fig. 2. Edge-on views of the central  $\text{B}_3\text{O}_3$  ring of (3) as viewed (a) nearly along the O1—O3 vector and (b) along the O2—B3 vector, revealing the distorted boat conformation produced by double intramolecular N—B chelation.

ble 2) relative to those at all others, revealing the former two to be the least affected by the chelations.

Reference compounds for other structural fragments of crystalline (3) include benzenboronic acid (Rettig & Trotter, 1977), its 4-bromo derivative (Zvonkova & Glushkova, 1958) and its 4-carboxy-2-nitro derivative (Soundararajan, Duesler & Hageman, 1993) as well as (1) itself and its *O*-methyl oxime (Scouten, Liu, Khangin, Mullica & Sappenfield, 1994). To our knowledge, only one *N,N*-dialkylated benzaldehyde hydrazone structure has been solved by crystallographic means, and that is a bis-condensation adduct of 4-methyl-2,6-diformylphenol with dimethyl *N,N'*-hydrazine diacetate (Kravtsov, Lozan, Simonov, Bologna, Gerbeleu & Malinovsky, 1994). In a fashion similar to that found for both *N,N*-dialkylhydrazone moieties in this structure,  $\pi$ -conjugation of the hydrazone fragment with the aromatic ring in (3) is facilitated by the near-zero [8.8 (5) $^\circ$ ] dihedral angle between the latter and the C20—C25—N5—N6 planar fragment. The N6 center in (3) is trigonally planar substituted and therefore *sp*<sup>2</sup> hybridized, and the sum of angles centered about it is 358.4 $^\circ$ . Those about the analogous N atoms in the reference 4-methyl-2,6-diformylphenol bis-dialkylhydrazone were determined to be 357.4 $^\circ$  ('A' side) and 348.6 $^\circ$  ('B' side). A doubly vinylogous connection of the electron-rich N6 center to the electron-poor B3 one in (3) undoubtedly enhances the  $\pi$ -conjugative connection of the (*E*)-hydrazone side chain to its pendant aromatic ring.

Each N and B involved in chelation in (3) is pyramidally substituted and therefore *sp*<sup>3</sup> hybridized and charge bearing. While the C1—B1 and C10—B2 bond lengths [1.595 (7) and 1.604 (7) Å, respectively] at the *sp*<sup>3</sup>-hybridized B centers are about the same as that found in (4) [1.602 (5) Å; Groziak, Ganguly & Robinson, 1994], the N4—B2 and N2—B1 bond lengths [1.678 (6) and 1.687 (6) Å, respectively] are longer by *ca* 0.1 Å, indicating that the N—B interactions in (3) are much weaker by comparison. It is noteworthy that, owing to their participation in chelation events, N2 and N4 cannot  $\pi$ -interact with their respective adjacent imine moieties. The N3—C16 imine double bond length of 1.262 (6) Å is somewhat shorter than the N1—C7 one [1.285 (6) Å] or either of those [1.282 (6) and 1.280 (6) Å] in the reference bis-hydrazone structure, a subtlety arising from slight differences in heterocycle ring puckerings.

An axis of local molecular symmetry about the B3—O2 vector renders the two chelation-derived benzodiazaborine rings spiro-fused onto the central B<sub>3</sub>O<sub>3</sub> ring roughly C<sub>2</sub> rotationally equivalent. Each of the 1,1,2,2-tetra-substituted 1,2-dihydro-2,3,1-benzodiazaborines exhibits a severe twist at the B—N site of saturation, as evidenced by the torsion angles N1—N2—B1—C1 and N3—N4—B2—C10 [−55.7 (5) and −51.8 (5) $^\circ$ , respectively], likely in alleviation of eclipsing interactions. The four substituents on this portion of the rings oc-

cupy near-perfect axial and equatorial positionings, as readily reflected in the dihedral angle values for O2—B2—N4—C18 and O2—B1—N2—C8 [−170.2 (4) and −174.4 (4) $^\circ$ , respectively]. Based on this striking structural feature in crystalline (3), it is now quite reasonable to suggest that a similar sort of ring pucker exists in the aqueous solution structure of (2).

## Experimental

2-Formylbenzenboronic acid (1) and 1,1-dimethylhydrazine were equilibrated for 5 h in 95% ethanol solution containing a catalytic amount of concentrated HCl at 298 K according to general procedures for the synthesis of benzodiazaborines from (1) and hydrazine reagents (Tschampel & Snyder, 1964; Dewar & Dougherty, 1964). The resulting white crystalline product was collected and washed in succession with water, 95% ethanol, acetone and diethyl ether to afford (3) in 88% yield. Recrystallization from dichloromethane gave X-ray quality crystals that had m.p. 489–491 K and exhibited low-resolution ACE (alternating CI/EI) mass spectral characteristics consistent with the solid-state structure described herein: EI, *m/e* 522.4 (40%, *M*<sup>+</sup>); CI, *m/e* 522.4 (100%, *M*<sup>+</sup>). Extensive <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectral analyses have shown (3) to exist in dry acetonitrile solution as a double intramolecular chelate likely related to that reported herein for the solid state, but in methanol solution as a single chelate, and in aqueous solution as the monomer (2).

### Crystal data

C<sub>27</sub>H<sub>33</sub>B<sub>3</sub>N<sub>6</sub>O<sub>3</sub>

*M<sub>r</sub>* = 522.03

Monoclinic

*P*2<sub>1</sub>/*n*

*a* = 14.505 (2) Å

*b* = 10.792 (1) Å

*c* = 18.496 (2) Å

$\beta$  = 98.81 (1) $^\circ$

*V* = 2861.1 (6) Å<sup>3</sup>

*Z* = 4

*D<sub>r</sub>* = 1.212 Mg m<sup>−3</sup>

*D<sub>m</sub>* not measured

Mo K $\alpha$  radiation

$\lambda$  = 0.71069 Å

Cell parameters from 25

reflections

$\theta$  = 10.03–11.00 $^\circ$

$\mu$  = 0.074 mm<sup>−1</sup>

*T* = 296 K

Prism

0.47 × 0.35 × 0.16 mm

Pale yellow

### Data collection

Rigaku AFC-5S diffractometer

$\omega$  scans (rate 6 $^\circ$  min<sup>−1</sup> in  $\omega$ , 3 repeats maximum)

Absorption correction:

none

5562 measured reflections

5340 independent reflections

1819 observed reflections

[*I* > 2 $\sigma$ (*I*)]

*R<sub>int</sub>* = 0.033

$\theta_{\max}$  = 25 $^\circ$

*h* = 0 → 17

*k* = 0 → 12

*l* = −21 → 21

3 standard reflections

monitored every 100

reflections

intensity decay: 0.2%

### Refinement

Refinement on *F*

*R* = 0.043

*wR* = 0.049

*S* = 1.49

( $\Delta/\sigma$ )<sub>max</sub> = 0.0003

$\Delta\rho_{\max}$  = 0.14 e Å<sup>−3</sup>

$\Delta\rho_{\min}$  = −0.15 e Å<sup>−3</sup>

Extinction correction: none

1819 reflections  
 352 parameters  
 H-atom parameters not  
 refined (riding, C—H =  
 0.95 Å)  
 $w = 4F_o^2/\sigma^2(F_o^2)$

Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV, Table  
 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
O1	0.6631 (2)	0.2220 (3)	0.87663 (16)	0.052 (1)
O2	0.78264 (18)	0.3066 (3)	0.96957 (15)	0.045 (1)
O3	0.64782 (19)	0.4269 (3)	0.91946 (15)	0.046 (1)
N1	0.9069 (3)	0.0922 (4)	0.9431 (2)	0.058 (2)
N2	0.8251 (3)	0.1352 (4)	0.8916 (2)	0.049 (1)
N3	0.8173 (3)	0.4983 (4)	1.0942 (2)	0.065 (2)
N4	0.7281 (3)	0.4724 (4)	1.0459 (2)	0.051 (1)
N5	0.4744 (3)	0.6688 (4)	0.7832 (2)	0.064 (2)
N6	0.5063 (4)	0.7832 (5)	0.8014 (3)	0.105 (2)
C1	0.7210 (3)	0.0910 (4)	0.9893 (2)	0.043 (2)
C2	0.7954 (3)	0.0186 (5)	1.0224 (2)	0.047 (2)
C3	0.7860 (4)	-0.0712 (5)	1.0747 (3)	0.068 (2)
C4	0.7015 (6)	-0.0909 (5)	1.0946 (3)	0.079 (2)
C5	0.6261 (4)	-0.0230 (7)	1.0633 (3)	0.079 (3)
C6	0.6353 (3)	0.0670 (5)	1.0116 (3)	0.061 (2)
C7	0.8858 (3)	0.0387 (5)	1.0005 (3)	0.062 (2)
C8	0.7909 (4)	0.0263 (5)	0.8460 (3)	0.070 (2)
C9	0.8630 (4)	0.2284 (5)	0.8452 (3)	0.075 (2)
C10	0.8076 (3)	0.5305 (4)	0.9350 (2)	0.049 (2)
C11	0.8771 (3)	0.5826 (5)	0.9858 (3)	0.061 (2)
C12	0.9417 (4)	0.6665 (6)	0.9653 (3)	0.082 (2)
C13	0.9362 (4)	0.7014 (6)	0.8938 (4)	0.090 (3)
C14	0.8677 (4)	0.6520 (6)	0.8425 (3)	0.080 (2)
C15	0.8049 (3)	0.5683 (5)	0.8628 (3)	0.060 (2)
C16	0.8791 (4)	0.5481 (6)	1.0626 (3)	0.073 (2)
C17	0.6836 (4)	0.3746 (5)	1.0850 (3)	0.067 (2)
C18	0.6710 (4)	0.5870 (5)	1.0449 (3)	0.073 (2)
C19	0.5215 (3)	0.3411 (4)	0.8188 (2)	0.038 (2)
C20	0.4750 (3)	0.4504 (4)	0.7933 (2)	0.044 (2)
C21	0.3916 (3)	0.4428 (5)	0.7448 (3)	0.061 (2)
C22	0.3528 (3)	0.3309 (6)	0.7214 (3)	0.068 (2)
C23	0.3973 (4)	0.2235 (5)	0.7448 (3)	0.062 (2)
C24	0.4805 (3)	0.2297 (4)	0.7928 (3)	0.051 (2)
C25	0.5125 (3)	0.5727 (5)	0.8150 (3)	0.052 (2)
C26	0.5762 (5)	0.8047 (5)	0.8619 (4)	0.101 (3)
C27	0.4527 (6)	0.8811 (6)	0.7679 (4)	0.121 (3)
B1	0.7422 (4)	0.1984 (6)	0.9349 (3)	0.045 (2)
B2	0.7415 (4)	0.4262 (5)	0.9615 (3)	0.043 (2)
B3	0.6156 (4)	0.3318 (6)	0.8748 (3)	0.042 (2)
N1—N2—B1	112.4 (3)	C24—C19—B3	116.8 (4)	
C8—N2—C9	109.1 (4)	C19—C20—C25	121.8 (4)	
C8—N2—B1	112.9 (4)	C21—C20—C25	118.7 (4)	
C9—N2—B1	110.8 (4)	N5—C25—C20	119.4 (4)	
N4—N3—C16	114.7 (4)	O1—B1—O2	114.4 (4)	
N3—N4—C17	104.2 (4)	O1—B1—N2	104.8 (4)	
N3—N4—C18	106.5 (4)	O1—B1—C1	112.6 (4)	
N3—N4—B2	113.7 (3)	O2—B1—N2	105.8 (4)	
C17—N4—C18	108.4 (4)	O2—B1—C1	114.8 (4)	
C17—N4—B2	111.3 (4)	N2—B1—C1	103.0 (4)	
C18—N4—B2	112.3 (4)	O2—B2—O3	113.8 (4)	
N6—N5—C25	121.5 (5)	O2—B2—N4	106.2 (4)	
N5—N6—C26	121.9 (5)	O2—B2—C10	114.2 (4)	
N5—N6—C27	115.8 (5)	O3—B2—N4	105.3 (4)	
C26—N6—C27	120.7 (6)	O3—B2—C10	112.6 (4)	
C2—C1—B1	118.3 (4)	N4—B2—C10	103.6 (4)	
C6—C1—B1	126.1 (4)	O1—B3—O3	121.1 (4)	
C1—C2—C7	117.7 (5)	O1—B3—C19	116.7 (5)	
C3—C2—C7	119.3 (5)	O3—B3—C19	122.2 (5)	
N1—C7—C2	129.7 (4)	O1—B1—O2—B2	12.6 (6)	
O1—B1—O2—B2	12.6 (6)	O1—B1—N2—N1	-173.6 (4)	
O1—B1—N2—N1	-173.6 (4)	O1—B1—N2—C8	-53.2 (5)	
O1—B1—N2—C8	-53.2 (5)	O1—B1—N2—C9	69.6 (5)	
O1—B1—N2—C9	69.6 (5)	O1—B3—O3—B2	11.3 (7)	
O1—B3—O3—B2	11.3 (7)	O1—B3—C19—C20	-161.7 (4)	
O1—B3—C19—C20	-161.7 (4)	O2—B1—O1—B3	-20.8 (6)	
O2—B1—O1—B3	-20.8 (6)	O2—B1—N2—N1	65.2 (5)	
O2—B1—N2—N1	65.2 (5)	O2—B1—N2—C8	-174.4 (4)	
O2—B1—N2—C8	-174.4 (4)	O2—B1—N2—C9	-51.6 (5)	
O2—B1—N2—C9	-51.6 (5)	O2—B2—O3—B3	-18.6 (6)	
O2—B2—O3—B3	-18.6 (6)	O2—B2—N4—N3	68.8 (5)	
O2—B2—N4—N3	68.8 (5)	O2—B2—N4—C17	-48.5 (5)	
O2—B2—N4—C17	-48.5 (5)	O2—B2—N4—C18	-170.2 (4)	
O2—B2—N4—C18	-170.2 (4)	O3—B2—O2—B1	5.8 (6)	
O3—B2—O2—B1	5.8 (6)	O3—B2—N4—N3	-170.2 (4)	
O3—B2—N4—N3	-170.2 (4)	O3—B2—N4—C17	72.5 (5)	
O3—B2—N4—C17	72.5 (5)	O3—B2—N4—C18	-49.2 (5)	
O3—B2—N4—C18	-49.2 (5)	O3—B3—O1—B1	9.5 (7)	
O3—B3—O1—B1	9.5 (7)	O3—B3—C19—C20	18.7 (7)	
O3—B3—C19—C20	18.7 (7)	N5—C25—C20—C19	170.9 (5)	
N5—C25—C20—C19	170.9 (5)	N6—N5—C25—C20	179.9 (5)	
N6—N5—C25—C20	179.9 (5)	C25—N5—N6—C26	-7.5 (9)	
C25—N5—N6—C26	-7.5 (9)	C25—N5—N6—C27	-173.6 (6)	
C25—N5—N6—C27	-173.6 (6)			

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH* and *PLATON* (Spek, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1192). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CHI 2HU, England.

Table 2. Selected geometric parameters (Å, °)

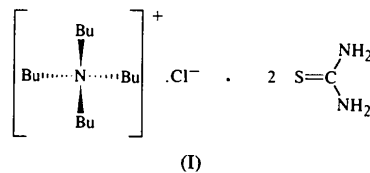
O1—B1	1.471 (6)	N4—B2	1.678 (6)
O1—B3	1.369 (6)	N5—N6	1.343 (6)
O2—B1	1.415 (6)	N5—C25	1.276 (5)
O2—B2	1.420 (6)	N6—C26	1.409 (7)
O3—B2	1.459 (5)	N6—C27	1.399 (7)
O3—B3	1.354 (6)	C1—C2	1.396 (6)
N1—N2	1.478 (5)	C1—B1	1.595 (7)
N1—C7	1.285 (6)	C2—C7	1.448 (6)
N2—C8	1.487 (6)	C10—C11	1.387 (6)
N2—C9	1.483 (6)	C10—B2	1.604 (7)
N2—B1	1.687 (6)	C11—C16	1.465 (7)
N3—N4	1.482 (5)	C19—C20	1.404 (6)
N3—C16	1.262 (6)	C19—B3	1.586 (6)
N4—C17	1.482 (6)	C20—C25	1.460 (6)
N4—C18	1.487 (6)		
B1—O1—B3	120.0 (4)	C11—C10—B2	119.0 (4)
B1—O2—B2	124.3 (4)	C15—C10—B2	124.7 (4)
B2—O3—B3	121.8 (4)	C10—C11—C16	117.3 (5)
N2—N1—C7	113.9 (4)	C12—C11—C16	120.9 (5)
N1—N2—C8	106.4 (3)	N3—C16—C11	130.3 (5)
N1—N2—C9	104.7 (4)	C20—C19—B3	126.4 (4)

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ered layers. However, in all four thiourea–halide lattices, each thiourea molecule interacts with adjacent thiourea molecules *via* N—H···S hydrogen bonds to give a ribbon-like arrangement, and also forms a pair of ‘chelating’ N—H···X hydrogen bonds with a halide ion; this results in an anionic framework or composite ribbon as a component in the crystal packing. As part of our ongoing investigation of the properties and molecular packing of adducts of thiourea/urea with peralkylated ammonium salts, the new adduct [(<sup>n</sup>C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>.Cl<sup>-</sup>].2[(NH<sub>2</sub>)<sub>2</sub>CS], (I), was prepared and characterized by single-crystal X-ray analysis.



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## Tetra-*n*-butylammonium Chloride–Thiourea (1/2), a Layer-Type Inclusion Compound

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### Abstract

The structure of a new layer-type inclusion compound, tetra-*n*-butylammonium chloride–thiourea (1/2), [(<sup>n</sup>C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>.Cl<sup>-</sup>].2[(NH<sub>2</sub>)<sub>2</sub>CS], is reported. The thiourea molecules and Cl<sup>-</sup> ions form nearly planar layers with the ordered tetra-*n*-butylammonium ions sandwiched between them. The layers, which correspond to the (101) family of planes, result from parallel hydrogen-bonded thiourea ribbons that are cross-bridged by Cl<sup>-</sup> anions.

### Comment

Several years ago, we reported the crystal structures of an isomorphous series of ternary complexes [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup>.X<sup>-</sup>].(NH<sub>2</sub>)<sub>2</sub>CO.2H<sub>2</sub>O (X = Cl, Br, CN) (Mak & McMullan, 1988) and a parallel study of a series of anhydrous adducts formed by thiourea and tetraalkylammonium halides (Mak, 1990). In the urea inclusion compounds, the cations are sandwiched between hydrogen-bonded urea–water–halide/pseudohalide pucker-

ed layers. Both independent thiourea molecules have normal planar configurations and dimensions (see, for example, Mak & Lau, 1978; Truter, 1967; Elcombe & Taylor, 1968). Each thiourea molecule couples with two neighbors related to it by a 2<sub>1</sub> screw axis to generate a slightly buckled ribbon running parallel to the *b* axis; these two resulting ribbons are each nearly planar, as indicated by the torsion angles C(1<sup>ii</sup>)—N(2<sup>ii</sup>)···S(1)—C(1) = -15.2(4) and C(1<sup>i</sup>)—N(1<sup>i</sup>)···S(1)—C(1) = -9.6(5)° for one ribbon and C(2<sup>iv</sup>)—N(3<sup>iv</sup>)···S(2)—C(2) = -5.9 and C(2<sup>v</sup>)—N(4<sup>v</sup>)···S(2)—C(2) = -2.2(5)° for the other. Adjacent ribbons are nearly coplanar and aligned in such a way that each has a thiourea molecule forming donor hydrogen bonds to the same Cl<sup>-</sup> ion in a bidentate chelating mode. The resulting puckered layer, which corresponds to the (101) family of planes, is thus generated by hydrogen-bonded thiourea ribbons and bridging Cl<sup>-</sup> ions. As shown in Fig. 1, an open octagon lies between a pair of Cl<sup>-</sup> ions in each layer. This thiourea–halide lattice can be contrasted with that of the compound [(<sup>n</sup>C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>(CH<sub>3</sub>)N<sup>+</sup>.Cl<sup>-</sup>].2[(NH<sub>2</sub>)<sub>2</sub>CS] (Mak, 1990) in which each thiourea ribbon is constructed from two independent thiourea molecules and the ribbons are arranged in a crisscross fashion.

A stereoview of the crystal structure is presented in Fig. 2. It can be seen that the ordered (<sup>n</sup>C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup> cations are sandwiched between hydrophilic layers with one alkyl leg pointing toward a neighboring octagonal void. The interlayer spacing is about 9.31 Å which is larger than the corresponding value for a similar layer structure with tetra-*n*-butylammonium cations accommodated in a urea–bicarbonate lattice {[(<sup>n</sup>C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>.HCO<sub>3</sub><sup>-</sup>].3[(NH<sub>2</sub>)<sub>2</sub>CO] (triclinic, 1/*a*\* = 8.32 Å; Li & Mak, 1995)}, as may be expected in view of the larger size of the S atom.