

terpretation of the 21 K phase transition; methyl hydrogen ordering is a possibility, if the acetate ions lie on twofold axes. On the other hand, the reported variability in the magnitude of the 21 K  $C_p$ -curve peak may well be related to the variability in diffraction pattern and domain size, found by us.

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## Sodium-Hydrogen and Boron-Hydrogen Interactions in the Cubane Structure of Tetrasodium Tetra- $\mu_3$ -hydrido-tetrakis(trimethylborate) Diethyl Ether Solvate, $[\text{NaB}(\text{CH}_3)_3\text{H}]_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}$

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**Abstract.**  $M_r = 393.8$ , monoclinic, space group  $P2_1/m$ ,  $a = 10.046$  (4),  $b = 10.81$  (3),  $c = 12.842$  (6) Å,  $\beta = 99.54$  (2)°,  $U = 1375.3$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 0.93$  (2),  $D_x = 0.95$  Mg m<sup>-3</sup>,  $\text{Cu } K\alpha$ ,  $\lambda = 1.54184$  Å,  $\mu = 0.868$  mm<sup>-1</sup>,  $F(000) = 436$ ,  $T = 133$  K,  $R = 0.105$  for 1252 observed reflections. The compound contains the tetrameric unit  $[\text{NaB}(\text{CH}_3)_3\text{H}]_4$ , as did the ether-free compound in benzene solution. The molecule is situated on a mirror plane giving a cubane structure of Na and H atoms. The structure thus consists of two interpenetrating tetrahedra of Na and hydridic H atoms at alternate corners of the very distorted cube. One of the Na atoms which lies on the mirror plane is coordinated to an ether molecule. Each hydridic H is bonded to the B of one trimethylboron group, thus forming a larger tetrahedron of B atoms. The tetrameric units are stacked along the  $b$  direction *via* interactions between the two Na atoms on the mirror plane and methyl H atoms of trimethylboron units in neighbouring tetramers. These chains are loosely held together in a two-dimensional network.

**Introduction.** Hydrides of the type  $\text{MBR}_3\text{H}$  ( $M = \text{alkali metal}$ ,  $R = \text{alkyl}$ ) are readily prepared from  $\text{MH}$  and  $\text{R}_3\text{B}$  (e.g. Brown & Krishnamurthy, 1978; Brown,

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Khuri & Kim, 1977; Honeycutt & Riddle, 1961) or from *tert*-BuLi and  $\text{R}_3\text{B}$  (Brown, Kramer, Hubbard & Krishnamurthy, 1980) and some are now commercially available ['Superhydride',  $R = \text{Et}$ ,  $M = \text{Li}$  (Brown & Krishnamurthy, 1973); 'L- and K-Selectride',  $R = \text{sec-Bu}$ ,  $M = \text{Li}$ , K (Brown & Krishnamurthy, 1972; Brown, 1973)]. These highly attractive reducing agents for organic synthesis are capable of achieving stereo- and regio-selective transformations unequalled by any other reagents currently available (Brown, Kim & Krishnamurthy, 1980; Ireland & Thompson, 1979; Walker, 1976). However, little is known about the nature of such reagents which have probably been assumed to contain the pseudotetrahedral hydrido-trialkylborate anion. We therefore examined the crystal structure of sodium hydridotrimethylborate. A preliminary report of this structure has appeared (Bell, Shearer & Spencer, 1980).

**Experimental.** Obtained from sodium hydride and trimethylboron in diethyl ether as reported earlier (Binger, Benedikt, Rotermund & Köster, 1968), recrystallized from hexane solution as colourless needles; drying in high vacuum gives solvent-free  $\text{NaB}(\text{CH}_3)_3\text{H}$ , which is tetrameric in benzene solution (Bell, Coates & Heslop, unpublished); crystalline needles, elongated along  $b$ , picked from hexane solution in a glove-box under an atmosphere of nitrogen without subjecting the crystals to high-vacuum drying and then individually sealed in thin-walled quartz capillary tubes in an atmosphere of dry nitrogen; X-ray analysis showed

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these to be the ether solvate  $[\text{NaB}(\text{CH}_3)_3\text{H}]_4 \cdot \text{Et}_2\text{O}$ .  $D_m$  by flotation. Crystals used were tapering needles,  $ca$   $0.25 \times 0.2 \times 0.9$  mm; the absence of diffraction data at  $\sin \theta > 0.5$  indicated the desirability of low-temperature data collection, so data were collected at 133 K using an apparatus based on that described by Robertson (1960) but modified for use with a horizontal equi-inclination Weissenberg goniometer. Lattice parameters determined from precession photographs. In the layers  $h0l$  to  $h6l$ , 1252 reflections were visually estimated, corrected for Lorentz and polarization factors and variation in spot length, not for absorption. From systematic absences, two space groups are possible,  $P2_1$  and  $P2_1/m$ ; unit cell contains two tetramer units, one per asymmetric unit for  $P2_1$  or half a molecule for  $P2_1/m$ , subsequent analysis proved more satisfactory in  $P2_1/m$ . Patterson function gave the positions of Na(1) and Na(2) lying on the mirror plane at  $y = 1/4$  with Na(3) below this plane and a symmetry-related atom, Na(3'), above; positions of the three B atoms and seven methyl C atoms, which with their symmetry-related atoms make up the tetramer, found from  $F_o$  synthesis phased on Na atoms;  $F_o - F_c$  synthesis showed a large peak near Na(1) and close to  $y = 1/4$ ; this was attributed to an ether O atom and neighbouring small peaks to the ether C atoms. Molecule could then be represented as  $[\text{NaB}(\text{CH}_3)_3\text{H}]_4 \cdot \text{Et}_2\text{O}$ , though at the outset of the structure determination the compound was believed to be the ether-free tetramer; subsequent refinement minimizing  $w^{1/2}\Delta^2$  ( $\Delta = F_o - F_c$ ) showed that the ether molecule is best considered disordered close to the mirror plane, with each molecule having a population factor of one half. In  $P2_1/m$ , with disordered ether atoms, difference map at  $R = 0.16$  showed three large peaks adjacent to the B atoms, interpreted as hydride H atoms. Positions of methyl H atoms were also indicated. Full-matrix refinement, anisotropic temperature factors for all non-hydrogen atoms except ether atoms, isotropic factors for all atoms of ether molecule and the hydride H atoms, but not refining the positions of the remaining hydrogens, converged at  $R = 0.105$ ; final  $F_o - F_c$  synthesis had largest peak of  $0.6 \text{ e } \text{\AA}^{-3}$ , on the mirror plane near one of the disordered carbons, maximum shift/error =  $0.40$ ,  $w = 1.0/(3.0 + |F_o| + 0.08|F_o|^2)$ , scattering factors from *International Tables for X-ray Crystallography* (1962).

**Discussion.** The atomic parameters are given in Table 1.\*

The crystal structure of  $\text{LiB}(\text{CH}_3)_4$  consists of planar sheets of alkali-metal atoms bridged by  $\text{B}(\text{CH}_3)_4$  groups

\* Structure factors, thermal parameters and a full list of H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38386 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional positional parameters ( $\times 10^4$ ) and isotropic thermal parameters with e.s.d.'s in parentheses

	x	y	z	$B(\text{\AA}^2)$
Na(1)	2248 (4)	2500	1625 (3)	5.1 (2)*
Na(2)	3929 (3)	2500	4280 (3)	4.6 (2)*
Na(3)	597 (2)	819 (3)	3550 (2)	3.5 (1)*
O†	3036 (7)	2237 (14)	66 (6)	4.3 (2)
B(1)	-987 (9)	2500	2221 (9)	3.8 (5)*
B(2)	1645 (8)	2500	5580 (7)	2.8 (4)*
B(3)	3163 (7)	355 (9)	2951 (6)	3.5 (4)*
C(1)	-1664 (9)	2500	3316 (8)	4.6 (6)*
C(2)	-1453 (7)	1251 (9)	1556 (5)	5.0 (4)*
C(3)	3237 (8)	2500	6155 (7)	3.7 (4)*
C(4)	891 (6)	1250 (8)	5905 (4)	3.7 (4)*
C(5)	4698 (7)	681 (9)	2796 (6)	4.7 (4)*
C(6)	3205 (7)	-538 (9)	4000 (7)	5.1 (4)*
C(7)	2291 (9)	-310 (11)	1940 (7)	6.8 (6)*
C(8)†	2128 (10)	2322 (33)	-924 (8)	4.7 (3)
C(9)†	733 (13)	2263 (30)	-671 (11)	6.3 (4)
C(10)†	4387 (16)	1961 (15)	-109 (13)	5.6 (4)
C(11)†	5137 (19)	2998 (18)	-488 (14)	7.2 (5)
H(1)	245 (68)	2500	2438 (54)	2.2 (15)
H(2)	1602 (82)	2500	4529 (65)	4.2 (21)
H(3)	2638 (48)	1231 (56)	3128 (36)	1.9 (10)

\*  $B_{\text{eq}}$  defined according to Willis & Pryor (1975).

† Atoms of the disordered ether molecule; population parameter 0.5.

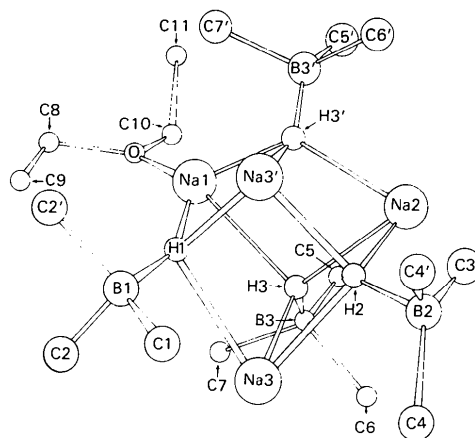


Fig. 1. Cubane structure of  $[\text{NaB}(\text{CH}_3)_3\text{H}]_4 \cdot \text{Et}_2\text{O}$  (C-H bonds omitted for clarity).

through linear  $\text{B}-\text{CH}_3-\text{Li}$  and multicentre fragments, though evidence for the existence of tetramers in the gas phase has been obtained from the mass spectrum of the compound (Rhine, Stucky & Peterson, 1975). In contrast, the crystal structure of  $[\text{NaB}(\text{CH}_3)_3\text{H}]_4 \cdot \text{Et}_2\text{O}$  contains a cubane arrangement of alternating Na and H atoms at the corners of a very distorted cube. Each H is bonded to the B of a  $\text{B}(\text{CH}_3)_3$  group as shown in Fig. 1. The four Na atoms lie at the corners of a tetrahedron and the four hydride H atoms at the corners of an interpenetrating but smaller tetrahedron, while the B atoms lie at the corners of a much larger tetrahedron. The basic cubane arrangement is much more distorted than that found for tetrameric methylzinc methoxide

(Shearer & Spencer, 1980). The basic cube is distorted such that the distances between the hydride H atoms which are all equal within the limits of experimental error and have a mean value of 2.73 (9) Å are much closer to each other than are the Na atoms [3.545 (5)–3.787 (4) Å]. This distortion can be described in terms of an inward movement of the H atoms along the threefold axes of the cube, resulting in the Na–H–Na angle being greater than 90° and the smallest angles being found at Na. Atoms Na(1) and Na(2) lie on the mirror plane at  $y = 1/4$  with Na(3) below this plane and a related atom above it. Similarly, B(1), B(2), H(1), H(2), C(1) and C(3) lie on this plane. The ether molecules are disordered but lie close to this plane, especially the O atom. This overall arrangement means that the hydride H atoms are 4-coordinate and three of the Na atoms in the tetrameric unit are 3-coordinate, Na(1) being 4-coordinate by virtue of the coordination of the ether molecule. Bond distances and bond angles are reported in Table 2 and some short contacts in Table 3.

The Na–Na distances are similar to the distances of 3.716 Å found in metallic sodium (*International Tables for X-ray Crystallography*, 1962) and in the dimer (NaBeEt<sub>2</sub>H·Et<sub>2</sub>O)<sub>2</sub> (3.620 Å) (Adamson, Bell & Shearer, 1981) but are longer than the interatomic distance for Na<sub>2</sub> in the gas phase (Herzberg, 1957). The seven crystallographically independent Na–H distances are not significantly different and lie in the range 2.25–2.42 Å with a mean value of 2.32 (5) Å, although the two Na–H distances in the mirror plane [Na(1)–H(1) and Na(2)–H(2)] are longest. The Na–H distances are less than the sum (3.03 Å) of the ionic radii (Pauling, 1960) and that found (2.440 Å) in NaH (Brewer & Mastick, 1951) but similar to those found (2.38, 2.41 Å) in (NaBeEt<sub>2</sub>H·Et<sub>2</sub>O)<sub>2</sub> (Adamson *et al.*, 1981) where H is also 4-coordinate. The B–H distances (1.13–1.34 Å) are all the same within experimental error and have a mean of 1.20 (7) Å, slightly longer than the sum of the covalent radii (Nordman & Lipscomb, 1953), as expected for electron-deficient bonding between B and H but similar to B–H bridging distances in B<sub>2</sub>H<sub>6</sub> [mean 1.24 (2) Å] (Smith & Lipscomb, 1965), B<sub>10</sub>H<sub>14</sub> [mean 1.21 (3) Å] (Nordman & Lipscomb, 1953) and Be(BH<sub>4</sub>)<sub>2</sub> [mean 1.14 (3) Å] (Marynick & Lipscomb, 1972). The B–C bond lengths are all equal within experimental error and have a mean value of 1.634 (11) Å similar to the B–C distances found [1.621–1.642, mean 1.632 (5) Å] from the X-ray study of LiB(CH<sub>3</sub>)<sub>4</sub> (Rhine *et al.*, 1975) and similar to the sum of the covalent radii (1.65 Å) (Pauling, 1960). Similarly, the two C–O distances do not differ significantly and have a mean value of 1.441 (16) Å, slightly longer than found in dimethyl ether (1.416 Å) (Kimura & Kubo, 1959). The C–C distances are similar and are normal. The Na–O distance of 2.290 (8) Å is shorter than that found in (NaBeEt<sub>2</sub>H·Et<sub>2</sub>O)<sub>2</sub> (Adamson *et al.*, 1981) where it is

Table 2. Bond distances (Å) and bond angles (°) with *e.s.d.*'s in parentheses

Symmetry code None $x, y, z$ ('') $x, 0.5-y, z$ ('') $-x, -y, 1.0-z$			
Na(1)–O	2.290 (8)	B(1)–H(1)	1.22 (7)
Na(1)–H(1)	2.42 (7)	B(2)–H(2)	1.34 (8)
Na(1)–H(3)	2.35 (5)	B(3)–H(3)	1.13 (6)
Na(2)–H(2)	2.41 (8)	B(1)–C(1)	1.660 (14)
Na(2)–H(3)	2.26 (5)	B(1)–C(2)	1.624 (11)
Na(3)–H(1)	2.30 (4)	B(2)–C(3)	1.647 (12)
Na(3)–H(2)	2.34 (5)	B(2)–C(4)	1.637 (9)
Na(3)–H(3)	2.25 (5)	B(3)–C(5)	1.625 (10)
O–C(8)	1.439 (13)	B(3)–C(6)	1.652 (12)
O–C(10)	1.443 (18)	B(3)–C(7)	1.610 (13)
C(8)–C(9)	1.492 (17)		
C(10)–C(11)	1.478 (25)		
H(1)–Na(1)–H(3)	71.5 (18)	H(1)–B(1)–C(1)	110.4 (27)
H(3)–Na(1)–H(3')	71.5 (18)	H(1)–B(1)–C(2)	108.2 (27)
H(2)–Na(2)–H(3)	67.9 (21)	H(2)–B(2)–C(3)	108.5 (29)
H(3)–Na(2)–H(3')	74.7 (19)	H(2)–B(2)–C(4)	108.5 (29)
H(1)–Na(3)–H(2)	74.2 (22)	H(3)–B(3)–C(5)	109.1 (27)
H(1)–Na(3)–H(3)	75.3 (19)	H(3)–B(3)–C(6)	106.0 (27)
H(2)–Na(3)–H(3)	69.3 (21)	H(3)–B(3)–C(7)	109.1 (27)
Na(1)–H(1)–Na(3)	102.4 (21)	H(1)–Na(1)–O	144.2 (14)
Na(3)–H(1)–Na(3')	104.3 (22)	H(3)–Na(1)–O	127.7 (13)
Na(2)–H(2)–Na(3)	105.7 (26)	H(3')–Na(1)–O	139.2 (13)
Na(3)–H(2)–Na(3')	101.8 (26)	Na(1)–O–C(8)	120.3 (11)
Na(1)–H(3)–Na(2)	100.5 (20)	Na(1)–O–C(10)	129.2 (9)
Na(1)–H(3)–Na(3)	106.2 (21)	C(8)–O–C(10)	110.5 (13)
Na(2)–H(3)–Na(3)	114.2 (22)	O–C(8)–C(9)	106.6 (17)
		O–C(10)–C(11)	116.0 (13)
Na(1)–H(1)–B(1)	141.8 (38)	C(1)–B(1)–C(2)	108.8 (6)
Na(3)–H(1)–B(1)	100.8 (32)	C(2)–B(1)–C(2')	112.4 (7)
Na(2)–H(2)–B(2)	105.3 (36)	C(3)–B(2)–C(4)	110.0 (5)
Na(3)–H(2)–B(2)	118.6 (40)	C(4)–B(2)–C(4')	111.3 (6)
Na(1)–H(3)–B(3)	110.2 (33)	C(5)–B(3)–C(6)	109.3 (6)
Na(2)–H(3)–B(3)	113.9 (34)	C(5)–B(3)–C(7)	113.5 (7)
Na(3)–H(3)–B(3)	111.0 (34)	C(6)–B(3)–C(7)	109.5 (7)

Table 3. Short contacts (Å) with *e.s.d.*'s in parentheses

(a) Intramolecular			
H(1)–H(3)	2.78 (8)	Na(2)–H(32)	2.277
H(2)–H(3)	2.61 (9)	Na(2)–H(52)	2.520
H(3)–H(3')	2.74 (9)	Na(2)–H(53)	2.866
H(1)–H(2)	2.80 (11)	Na(2)–H(61)	2.907
Na(1)–Na(2)	3.545 (5)	Na(3)–H(12)	2.357
Na(1)–Na(3)	3.677 (4)	Na(3)–H(21)	2.497
Na(2)–Na(3)	3.787 (4)	Na(3)–H(41)	2.782
Na(3)–Na(3')	3.635 (5)	Na(3)–H(42)	2.826
Na(1)–H(53)	2.723 (3)	Na(3)–H(62)	2.467
Na(1)–H(71)	2.636 (1)	Na(3)–H(72)	2.618
(b) Intermolecular			
Na(3)–H(41'')	2.708		
Na(3)–H(42'')	2.556		
Na(3)–H(43'')	2.730		

equal to the sum of the ionic radii (2.350 Å) (Pauling, 1960).

The seven independent Na–H–Na angles range from 100.5 (20) to 114.2 (22)°, the larger angles being accounted for by the slightly longer Na–H distances in the mirror plane. The H–Na–H angles are the same within experimental error ranging from 67.9 (21) to 75.3 (19)° with a mean of 71.9 (20)°. The Na–H–B angles at H(2), H(3) and H(3') are all equal with a mean value of 112.5 (37)°. At H(1), Na(1)–H(1)–B(1) is 142 (4)° compared with 101 (3)° for Na(3)–H(1)–B(1) owing to the presence of hydrogen attached to C(9). The seven independent

H—B—C angles are approximately tetrahedral [106.0 (27)–110.4 (27)°], whereas the three independent H—Na—O angles vary between 127.7 (13) and 144.2 (14)° and the two Na—O—C angles are 120.3 (11) and 129.2 (9)°, while the C—O—C angle [110.5 (13)°] is close to tetrahedral. The sums of the C—O—C and C—O—Na angles are 360 (3)° and thus the O atom lies in the plane of the three atoms to which it is bonded.

The structure is therefore considered as being made up of cubane units with highly polar Na—H bonds. All four Na atoms interact with three hydride H atoms while Na(1) is also coordinated to the O of an ether molecule. The hydridic H atoms have as neighbours one B and three Na atoms arranged tetrahedrally. In addition there are some relatively short inter- and intramolecular Na—methyl H-atom interactions and those contacts less than 3.0 Å are listed in Table 3 together with the Na...Na and H...H distances in the cubane framework. For the intramolecular contacts which appear to result from the close approach of the Me<sub>3</sub>B units to the hydridic H atoms, both Na(3) and Na(3') have six contacts less than 3.0 Å and Na(2) has eight whereas the more sterically crowded Na(1) has only four distances in this range, to H(53), H(71), and their symmetry-related atoms.

The tetrameric units are packed along **b** (Fig. 2) resulting in some short intermolecular contacts between Na(3), Na(3') and methyl H atoms of neighbouring tetramers and this may well also account for the observed distortion of the cubane structure. Both of the symmetry-related sodium atoms, Na(3) and Na(3'),

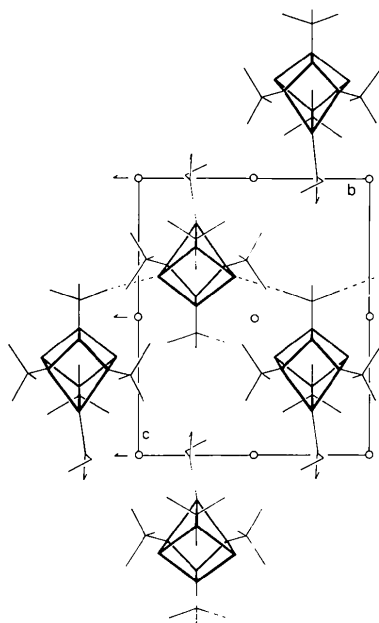
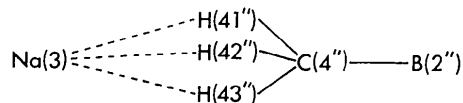


Fig. 2. View along  $a^*$  showing the stacking along **b**. Intermolecular contacts are represented by dotted lines.

have three intermolecular contacts in the range 2.556–2.730 Å with all three H atoms attached to C(4'') and C(4''')\* respectively. This umbrella arrangement



is similar to those in tetrameric methyl lithium (Weiss & Lucken, 1964; Weiss & Hencken, 1970) and in LiBMe<sub>4</sub> (Rhine *et al.*, 1975). In addition these chains are weakly held by somewhat longer intermolecular interactions between Na(2) and two methyl H atoms on different molecules (3.24 Å), thereby giving a loosely held two-dimensional network parallel to the *ab* plane.

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\* C(4''') is related to C(4'') by the mirror plane at  $y = 1/4$ .

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**[1,9-Bis(diphenylphosphino)-3,7-dithianonane]monobromonickel(II) Tetraphenylborate, C<sub>31</sub>H<sub>34</sub>BrNiP<sub>2</sub>S<sub>2</sub><sup>+</sup>·C<sub>24</sub>H<sub>20</sub>B<sup>-</sup>, at 295 K, and [1,9-Bis(diphenylphosphino)-3,7-dithianonane]monoiodonickel(II) Tetraphenylborate, C<sub>31</sub>H<sub>34</sub>INiP<sub>2</sub>S<sub>2</sub><sup>+</sup>·C<sub>24</sub>H<sub>20</sub>B<sup>-</sup>, at 120 K\***

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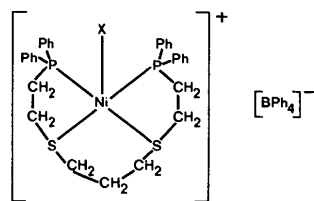
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**Abstract.** [Ni(C<sub>31</sub>H<sub>34</sub>P<sub>2</sub>S<sub>2</sub>)Br] [B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]:  $M_r = 990.53$ ,  $Pn$ ,  $a = 14.472$  (2),  $b = 10.0092$  (9),  $c = 16.573$  (2) Å,  $\beta = 94.61$  (1)°,  $V = 2393$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.37$ ,  $D_x = 1.375$  Mg m<sup>-3</sup>,  $Cu K\alpha$ ,  $\lambda = 1.54056$  Å,  $\mu = 3.34$  mm<sup>-1</sup>,  $T = 295$  K,  $R = 0.085$ ,  $wR = 0.108$ , 3085 unique reflexions. [Ni(C<sub>31</sub>H<sub>34</sub>P<sub>2</sub>S<sub>2</sub>)I] [B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]:  $M_r = 1037.53$ ,  $Pn$ ,  $a = 14.381$  (3),  $b = 9.886$  (1),  $c = 16.510$  (3) Å,  $\beta = 94.31$  (1)°,  $V = 2341$  Å<sup>3</sup>,  $Z = 2$ ,  $Mo K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 1.23$  mm<sup>-1</sup>,  $T = 120$  K,  $R = 0.078$ ,  $wR = 0.100$ , 2336 unique reflexions. The isostructural title compounds are built up of discrete [Ni(C<sub>31</sub>H<sub>34</sub>P<sub>2</sub>S<sub>2</sub>)X]<sup>+</sup> and [B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sup>-</sup> ions, X = Br and I. In the square-pyramidal cations a single ligand molecule, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>S(CH<sub>2</sub>)<sub>3</sub>S(CH<sub>2</sub>)<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, denoted pssp is coordinated to one Ni *via* the P and S atoms thus forming two five-membered (NiPC<sub>2</sub>S) and one six-membered (NiSC<sub>3</sub>S) chelate rings. The P and S atoms constitute the basal plane in the square pyramid and the halide atom is situated at the apex. All interatomic distances and angles are normal. [Ni(pssp)Br] [BPh<sub>4</sub>] (Ph = C<sub>6</sub>H<sub>5</sub>) is diamagnetic. [Ni(pssp)I] [BPh<sub>4</sub>] is diamagnetic at 120 K but shows temperature-independent paramagnetism at 295 K.

**Introduction.** Five-coordinated Ni<sup>II</sup> complexes with linear open-chain ligands, like pssp, are often of square-pyramidal type (Morassi, Bertini & Sacconi, 1973). According to Orioli (1971) the spin state of the Ni<sup>2+</sup> ion in the complex depends on the electronegativity of the coordinated donor atoms. Complexes with low electronegative donors, such as P and S, are most often diamagnetic. The stereochemical activity of

the filled  $d_{z^2}$  orbital of low-spin Ni<sup>II</sup> causes the Ni–apical-ligand distance in the square pyramid to be longer than analogous Ni–basal-ligand distances. The Ni–basal-ligand distances are comparable with similar four-coordinated square-planar distances. The Ni-atom displacement from the basal plane towards the apical-ligand atom is smaller than in high-spin complexes where it is of the order 0.3–0.4 Å.

The crystal structure of [Ni(pssp)I] [BPh<sub>4</sub>] has been determined at 295 K (Aurivillius & Bertinsson, 1980). This compound shows magnetic phase transitions in the temperature interval 80–290 K and there is a colour change from dark red to light brown ~150 K on cooling. The structure determinations of [Ni(pssp)Br] [BPh<sub>4</sub>] at 295 K and [Ni(pssp)I] [BPh<sub>4</sub>] at 120 K



were undertaken to study possible differences in the coordination polyhedra and in the Ni–ligand distances and angles. This investigation is part of a more general study of complexes between transition-metal halides and substituted phosphines or related ligands.

**Experimental.** Values of [Ni(pssp)Br] [BPh<sub>4</sub>], and for [Ni(pssp)I] [BPh<sub>4</sub>] at 120 K in parentheses if they differ, are given. Dark-red crystals in the form of plates,  $D_m$  by flotation, 0.12 × 0.22 × 0.12 mm (0.19 × 0.27 × 0.08 mm), Enraf–Nonius CAD-4 diffractometer.  $Cu K\alpha$ , Ni filter, (Mo  $K\alpha$ , Zr filter), cell parameters from 49 (50) accurately measured  $\theta$  values,

\* Structures of Complexes between Metal Halides and Phosphinothioethers or Related Ligands. XV.