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2,2′-Bipyridyl and 1,10-phenanthroline adducts of the diborane(4) compound $B_2(1,2\text{-}S_2C_6H_4)_2$

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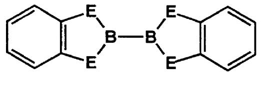
Abstract—The syntheses and structures of the 2,2′-bipyridyl and 1,10-phenanthroline adducts of the diborane(4) compound $B_2(1,2\text{-}S_2C_6H_4)_2$ are described. In both cases, the bidentate nitrogen donor ligands bridge the B–B bond, one nitrogen being bonded to each boron. © 1998 Elsevier Science Ltd. All rights reserved

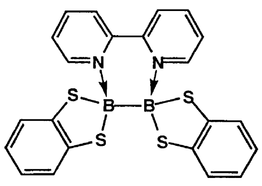
Keywords: diborane(4); ligand adducts.

INTRODUCTION

Diborane(4) compounds, B_2R_4 (for a recent overview containing key references, see Ref. [1]), have been the focus of renewed interest in recent years, not least because of their importance as reagents in transition metal catalysed diboration reactions [2], and as part of our own interest in such compounds, we have recently reported results relating to the Lewis acidity of the boron centres [3, 4]. Specifically, we noted that the compounds $B_2(cat)_2$ (**1**) (cat = $1,2\text{-}O_2C_6H_4$) and $B_2(thiocat)_2$ (**2**) (thiocat = $1,2\text{-}S_2C_6H_4$) [5, 6] formed both *mono* and *bis*-adducts with 4-picoline [3, 4], whilst **2** also formed *mono* and *bis*-adducts with tertiary phosphines consistent with a greater degree of Lewis acidity for the sulphur substituted boron centres [4]. Herein, we describe the adducts formed between **2** and 2,2′-bipyridyl and 1,10-phenanthroline.



1, E = O; **2**, E = S



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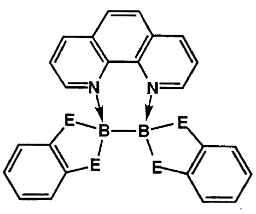

4, E = S; **5**, E = O

RESULTS AND DISCUSSION

Reactions between **2** and one equivalent of either 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen) in CH_2Cl_2 solution led to the immediate formation of a

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coloured (pale red in the case of **3** and red in the case of **4**) solution. After addition of an overlayer of toluene and subsequent solvent diffusion over a period of days at −30°C, dark red (almost black in the case of **4**) crystals were obtained, analytical data for which were in accord with the formulae [B_2(thiocat)$_2$(bipy)] (**3**) and [B_2(thiocat)$_2$(phen)] (**4**) (in both cases, with some solvent of crystallisation: see Experimental section).

Single crystals of both **3** and **4**, although of relatively poor quality, were suitable for X-ray crystallography, the results of which are shown in Figs 1 and 2 with selected bond lengths and angles given in Table 1. Compound **3** (Fig. 1) crystallises as a CH_2Cl_2 solvate with two molecules of **3** and two of CH_2Cl_2 in the asymmetric unit. The independent molecules of **3** are essentially identical (they are related by a pseudo-inversion centre; see Experimental section) and consist of units of **2** with the bipy ligand bridging the B–B bond, one nitrogen centre being bonded to each boron. The two B–B distances [B(1)–B(2) 1.65(5) and B(3)–B(4) 1.61(4) Å] are the same within experimental error and similar both to the B–B distance in **2** itself [1.673 Å average for two independent molecules] [6] and to the corresponding bond lengths in the related *bis*-adduct compounds of **2** [B_2(thiocat)$_2$(4-picoline)$_2$] [B–B 1.715(10) Å] and [B_2(thiocat)$_2$(PMe_2Ph)$_2$] [B–B 1.750(4) Å] [4]. The B–S distances in **3** (average 1.916 Å) are similar to those found in [B_2(thiocat)$_2$(4-picoline)$_2$] and [B_2(thiocat)$_2$(PMe_2Ph)$_2$] and the B–N bond lengths (average 1.65 Å) are also similar to those found in both the *mono* and *bis*-4-picoline adducts of **1** and **2** described in Refs. [3, 4]. All boron atoms in **3** are tetrahedrally coordinated with angles which do not deviate markedly from ideal values; any deviations which are present are likely to arise from constraints imposed by the five and six-membered rings. The coordination of the bipy ligands does, however, result in a significant twisting about the B–B bond leading to an ethane-like conformation for the (BS_2N)$_2$ unit. Thus the torsion angles defined by taking the coordinates of the mid-point of the S–S vectors in each thiocat group and the two boron atoms are 64.9 and 51.4°. The $B_2N_2C_2$ six-membered rings are markedly non-planar [τ(NBBN) = 50.2 and 50.4°; τ(NCCN) = 14.2 and 29.2°, maximum deviation from $B_2N_2C_2$ plane is 0.32 Å for B(2) and 0.35 Å for B(4)].

Compound **4** crystallises as a CH_2Cl_2 and toluene solvate with molecules of **4** lying on a crystallographic C_2 axis. The molecular structure of **4** (Fig. 2) is similar to that of **3** in that the phen ligand bridges the B–B bond of the B_2(thiocat)$_2$ unit. The B–B [1.707(13) Å], B–S [B(1)–S(1) 1.903(7) and B(1)–S(2) 1.930(7) Å] and B–N [B(1)–N(1) 1.620(8) Å] distances are all in expected ranges when compared with those of **3** and the compounds described in Ref. [4] and the twisting about the B–B bond seen in **3** is also present here [equivalent torsion angles and interplanar angles defined as above are: 38.1° for "S"BB"S"; τ(NBBN) = 35.2°; τ(NCCN) = 7.1°, maximum deviation from $B_2N_2C_2$ plane is 0.22 Å for B(1) and B(1a)].

Perhaps the most unusual feature about **3** and **4** is the observation that the bipy and phen ligands bridge an element–element bond. This type of bridging coordination is extremely rare for these ligands, the only previously known examples being the double quat-

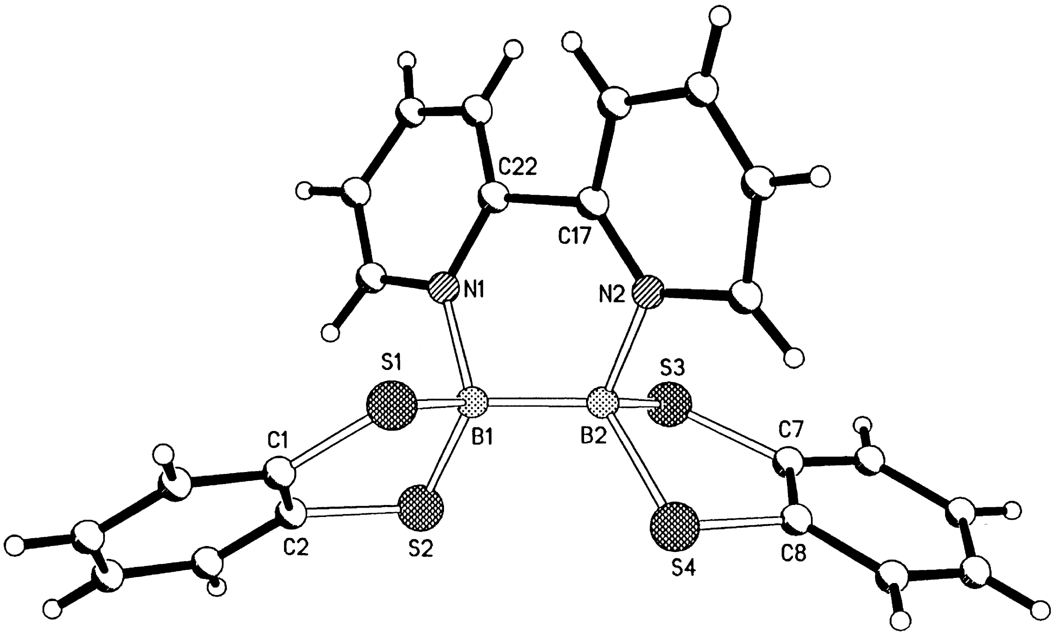

Fig. 1. A view of the molecular structure of one of the two crystallographically independent molecules of **3** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

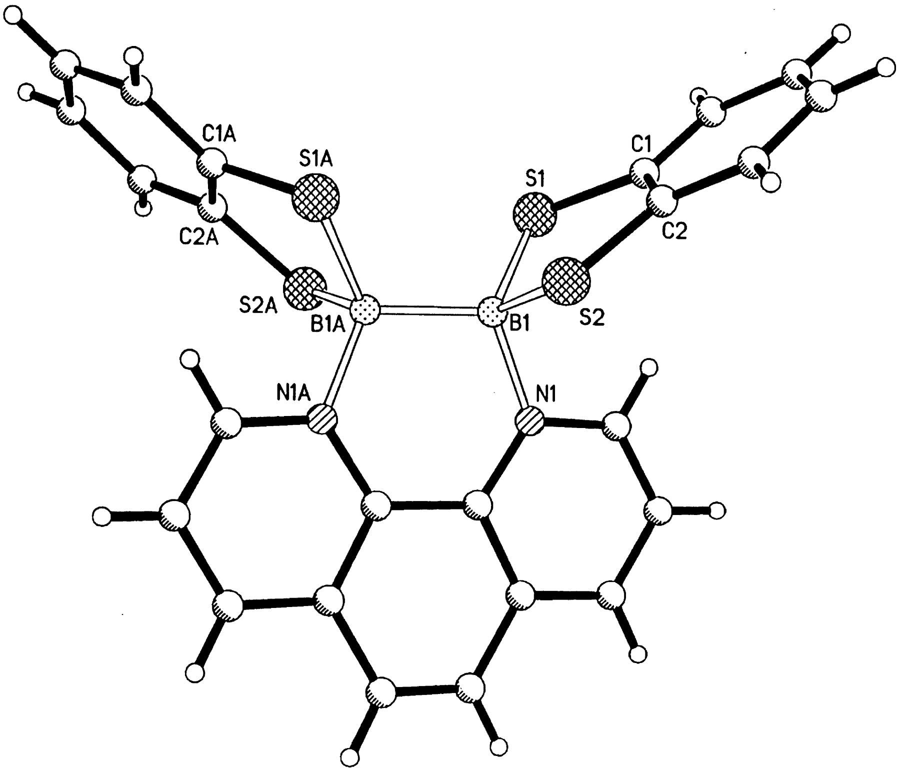

Fig. 2. A view of the molecular structure of **4** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths and angles for compounds **3** and **4**

3[a]		**3**[a]		**4**	
Bond lengths					
B(1)–B(2)	1.65(5)	B(3)–B(4)	1.61(4)	B(1)–B(1a)	1.707(13)
B(1)–S(1)	1.95(4)	B(3)–S(5)	1.93(3)	B(1)–S(1)	1.903(7)
B(1)–S(2)	1.83(4)	B(3)–S(6)	1.90(3)	B(1)–S(2)	1.930(7)
B(1)–N(1)	1.65(4)	B(3)–N(3)	1.68(4)	B(1)–N(1)	1.620(8)
B(2)–S(3)	1.95(3)	B(4)–S(7)	1.94(3)		
B(2)–S(4)	1.95(3)	B(4)–S(8)	1.94(3)		
B(2)–N(2)	1.68(3)	B(4)–N(4)	1.61(3)		
Bond angles					
B(2)–B(1)–S(1)	113(2)	B(4)–B(3)–S(5)	117(2)	B(1a)–B(1)–S(1)	110.6(4)
B(2)–B(1)–S(2)	115(2)	B(4)–B(3)–S(6)	115(2)	B(1a)–B(1)–S(2)	114.5(5)
B(2)–B(1)–N(1)	105(2)	B(4)–B(3)–N(3)	106(2)	B(1a)–B(1)–N(1)	110.2(3)
N(1)–B(1)–S(1)	104(2)	N(3)–B(3)–S(5)	106(2)	N(1)–B(1)–S(1)	111.1(4)
N(1)–B(1)–S(2)	114(2)	N(3)–B(3)–S(6)	108(2)	N(1)–B(1)–S(2)	105.5(4)
S(1)–B(1)–S(2)	106(2)	S(5)–B(3)–S(6)	103.6(14)	S(1)–B(1)–S(2)	104.8(3)
B(1)–B(2)–S(3)	113(2)	B(3)–B(4)–S(7)	116(2)		
B(1)–B(2)–S(4)	118(2)	B(3)–B(4)–S(8)	115(2)		
B(1)–B(2)–N(2)	111(2)	B(3)–B(4)–N(4)	109(2)		
N(2)–B(2)–S(3)	107(2)	N(4)–B(4)–S(7)	106(2)		
N(2)–B(2)–S(4)	106(2)	N(4)–B(4)–S(8)	108(2)		
S(3)–B(2)–S(4)	100.5(13)	S(7)–B(4)–S(8)	101.8(12)		

[a] Two crystallographically independent molecules.

ernary, *N*,*N*′-dialkyl species formed by reaction between either bipy or phen and 1,2-dibromoethane [7].

Also interesting is the colour of these two complexes. All of the *mono* and *bis*-picoline adducts of **1** and **2** described in Refs. [3, 4] are colourless or very pale yellow in contrast to the red colours seen here. These are presumably charge-transfer transitions from filled orbitals in the B_2(thiocat)$_2$ unit to empty π^*-orbitals of the bipy or phen ligands. That the colours persist in solution indicates that association between **2** and either bipy or phen is present in solution as well as in the solid state although we were not able to confirm this by ^{1}H or ^{11}B NMR studies owing to the very poor solubility of both **3** and **4**.

As a final point, we note that **1** also forms a red solution in $CHCl_3$ when one equivalent of 1,10-phenanthroline is added, with red crystals being isolated after work-up. On the basis of the colour of the solution and solid, a similar structure to **4** is likely but since the crystals were not of X-ray quality, any structural formulation must remain tentative although analytical data were consistent with the formation of a 1:1 adduct albeit as a $CHCl_3$ solvate.

EXPERIMENTAL

General procedures

All reactions were performed using standard Schlenk techniques under an atmosphere of dry, oxygen-free dinitrogen. All solvents were distilled from appropriate drying agents immediately prior to use (sodium for toluene and hexanes and CaH_2 for CH_2Cl_2). Microanalytical data were obtained at the University of Bristol and UV-visible spectra were obtained on a Perkin-Elmer Lambda 2 spectrophotometer.

Compounds **1** and **2** were prepared by the literature methods [5]. 2,2′-bipyridyl and 1,10-phenanthroline were procured commercially but were dried by azeotropic distillation of toluene in a Dean and Stark apparatus before use.

Preparations

[B_2(thiocat)$_2$(phen)] (4) A solution of dried 1,10-phenanthroline (0.029 g, 0.16 mmol) in CH_2Cl_2 (2 cm^3) was added to a stirred solution of **2** (0.050 g, 0.16 mmol) in CH_2Cl_2 (2 cm^3) resulting in the immediate formation of a red solution. Addition of an overlayer of toluene (3 cm^3), cooling to -30°C and subsequent solvent diffusion over a period of two days afforded **4** as dark red (almost black) crystals which were then washed with hexane (2×2 cm^3) (0.089 g, 84%). One of these crystals was used for X-ray crystallography which revealed the presence of one molecule of CH_2Cl_2 and one molecule of toluene per molecule of **4**. $C_{24}H_{16}N_2B_2S_4\cdot CH_2Cl_2\cdot C_6H_5CH_3$ requires C, 58.30; H, 4.00; N, 4.20%. Found: C, 56.10; H, 3.70; N, 4.80. Some loss of solvent of crystallisation occurred accounting for the poor quality analytical data. UV-VIS (CH_2Cl_2), 509.8 nm, $\varepsilon_0=26$.

Compound **3** was prepared in an analogous manner and in similar yield using 2,2′-bipyridyl in place of 1,10-phenanthroline. X-ray crystallography revealed the presence of CH_2Cl_2 of crystallisation. $C_{22}H_{16}N_2B_2S_4\cdot CH_2Cl_2$ requires C, 50.90; H, 3.35; N, 5.15%. Found: C, 50.65; H, 3.15; N, 5.05. The pale red colour of solutions of **3** in CH_2Cl_2 were not of a sufficient intensity to obtain satisfactory solution UV-VIS data.

Compound **5** was also prepared similarly but using $CHCl_3$ rather than CH_2Cl_2. Analytical data were consistent with a 1:1 adduct of **1** and 1,10-phenanthroline with one molecule of $CHCl_3$ of crystallisation present. $C_{24}H_{16}N_2B_2O_4\cdot CHCl_3$ requires C, 55.90; H 3.20; N, 5.20%. Found: C, 55.05; H, 3.00; N, 4.45. UV-VIS (CH_2Cl_2), $\lambda=425.0$ nm, $\varepsilon_0=540$.

It is important that the 2,2′-bipyridyl and 1,10-phenanthroline used in these reactions is dry and that none of the hydrates are present. Any traces of water lead to extensive decomposition products, one of which, in the reaction which afforded **5**, was identified by X-ray crystallography as the salt $[\text{phenH}]^+[\text{B(cat)}_2]^-$ [8].

X-ray crystallography

Crystal data for $3\cdot CH_2Cl_2$ $C_{23}H_{18}B_2Cl_2N_2S_4$, $M=543.15$, orthorhombic, $a=16.828(3)$, $b=14.553(3)$, $c=20.069(4)$ Å, $U=4914.9(17)$ Å^3, $T=220(1)$ K, space group $Pna2_1$ (No. 33), $Z=8$, $\mu=0.62$ mm^{-1}, 3062 reflections measured, 2475 unique ($R_{\text{int}}=0.0970$). Final $R_1=0.0830$ for 1849 reflections $I>2\sigma(I)$.

X-ray diffraction measurements were made on a single crystal mounted on a glass fibre with graphite-monochromated Mo-K$_\alpha$ X-radiation ($\lambda=0.71073$ Å) using a Rigaku AFC7S diffractometer. Unit cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 18 carefully centred reflections in the range $7.31° < \theta < 11.49°$. Intensity data were collected using the ω–2θ scan technique. Azimuthal scans of several reflections indicated no need for an absorption correction. Data were integrated using teXsan [9] and were corrected for Lorentz and polarisation effects. Intensities were weak and collected to only $\theta=20.26°$. The structure was solved by direct methods and refined by full-matrix least squares against F^2 for all data with $I>-3\sigma(I)$. The structure was solved and refined in the acentric space group $Pna2_1$ with two molecules of **3** and two dichloromethane solvent molecules per asymmetric unit. There appears to be a local pseudo inversion centre between the molecules of **3** although this does not hold for the solvent molecules and is not a true inversion centre. Chlorine, sulphur and nitrogen atoms were refined anisotropically and hydrogens were assigned fixed isotropic displacement parameters and were constrained to idealised geometries. The aromatic rings of the $BS_2C_6H_4$ groups were restrained to D_{6h} symmetry. The absolute structure parameter [10] was determined by refinement to be $-0.10(40)$.

Crystal data for $\mathbf{4}\cdot 1.0CH_2Cl_2 1.0C_6H_5Me$ $C_{16}H_{13}BClNS_2$, $M=329.65$, monoclinic, $a=12.332(3)$, $b=10.1552(13)$, $c=12.259(2)$ Å, $\beta=90.108(10)^\circ$ $U=1535.1(4)$ Å^3, $T=173(2)$ K, space group $P2/c$ (No. 13), $Z=4$, $\mu=0.51$ mm^{-1}, 9230 reflections measured, 3498 unique ($R_{int}=0.0308$). Final $R_1=0.0898$ for 2974 reflections $I>2\sigma(I)$.

Many of the details of the structure analyses are the same as those for **3**·CH_2Cl_2. X-ray diffraction measurements on a single crystal coated in a hydrocarbon oil mounted on a glass-fibre under argon were made using a Siemens SMART diffractometer. Intensity data were collected by 0.3° width ω steps accumulating area detector frames spanning a hemisphere of reciprocal space. Data were integrated using the SAINT [11] program and corrected for Lorentz, polarisation and long-term intensity fluctuations. The asymmetric unit contained half a molecule of **4**, CH_2Cl_2 and C_6H_5Me, with molecules of **4** lying over a crystallographic C_2 axis. The toluene and dichloromethane solvates were disordered over an inversion centre. Since the β angle was 90.108° the structure was refined to test the possibility that it may be twinned with a pseudo-orthorhombic cell, using the twin law $(1\,0\,0, 0\,-1\,0, 0\,0\,-1)$. However, the twin component parameter refined to 0.012(2) indicating a marginal amount of twinning and resulted in no significant improvement in the R-factor. An extinction parameter, x, of the form $F_c'=F_c/[1+0.001xF_c^2\lambda^3/\sin(2\theta)]^{-0.25}$ was refined to 0.014(2). All calculations were made with programs of the SHELXTL system [12]. Complex neutral-scattering factors were taken from Ref. [13].

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