ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 585 (1999) 127–133

Journal of Organo metallic Chemistry

Syntheses and solid-state structures of mono- and dialkyl(methylsulfonato)boranes

Rainer Papp, Fernando B. Somoza Jr., Joachim Sieler, Steffen Blaurock,
Evamarie Hey-Hawkins *

Institut für Anorganische Chemie der Universität Leipzig, Talstrasse 35, D-04103 Leipzig, Germany

Received 20 February 1999; received in revised form 8 April 1999

Abstract

R_3B reacts with $MeSO_3H$ at elevated temperature in toluene to give liquid $R_2B(OSO_2Me)$ [R = Et (**1a**), 61%; R = Bu (**1b**), 58%; R = Pr^i (**1c**), 23%] and, in the case of Et_3B and Bu_3B, solid $RB(OSO_2Me)_2$ [R = Et (**2a**), 13%; R = Bu (**2b**), 11%]. As Pr^i_3B is less reactive, pivalic acid must be added as catalyst, and no formation of the disulfonatoborane is observed. Complexes **1a**–**c** and **2a**–**b** were characterised spectroscopically (IR, ^1H-, ^{13}C-, ^{11}B-NMR), and crystal structure determinations were carried out on **1a**, which is monomeric even in the solid state, and **2a** and **2b**, which are dimeric in the solid state and have two differently bonded sulfonate groups (terminal and bridging). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Boranes; Alkyldi(methylsulfonato)boranes; Dialkyl(methylsulfonato)boranes; Crystal structure

1. Introduction

In our ongoing studies on potential boranyl (BR_2) and boranediyl (BR) precursors [1], we are interested in the synthesis and solid-state structures of boron reagents with reactive boron-substituent bonds, as these are interesting starting materials for the preparation of transition metal–boron complexes [2]. Since the intramolecularly base-stabilised aryl–BCl_2 derivatives synthesised previously in our group [1b] did not react with anionic transition metal complexes, we investigated the use of alkyl(sulfonato)boranes for this purpose. While the sulfonato group is well known in organic chemistry, where it is used as a good leaving group, it has rarely been used in inorganic chemistry. As early as 1969, Trofimenko prepared the first dialkylboron sulfonates from various sulfonic acids and trialkylboranes and showed that these compounds are useful starting materials for the preparation of alkyl(amino)boranes [3], especially pyrazaboles [3,4]. Since then, several dialkylboron triflates and mesylates have been designed and used for the stereoselective enolboration of ketones in the presence of amines [5–7]. Other known sulfonatoboranes [8–12] include the structurally characterised *nido*-6-CF_3SO_3–$B_{10}H_{13}$ [8] and $B_2(NMe_2)_2(tosylate)_2$ [9], as well as the dichloro(sulfonato)boranes, $Cl_2B(OSO_2R)$ (R = Me, Et, *p*-tol) [12], which were, however, only characterised by elemental analyses. The use of sulfonatoboranes in transition metal chemistry has not yet been reported.

We now report the syntheses of $R_2B(OSO_2Me)$ [R = Et (**1a**) [3a], Bu (**1b**), Pr^i (**1c**)] and $RB(OSO_2Me)_2$ [R = Et (**2a**), Bu (**2b**)] and the solid-state structures of **1a**, **2a** and **2b**.

There are approximately 100 structurally characterised compounds with sulfonato ligands listed in the Cambridge Crystallographic Data Centre. Of these, those with terminal (η^1) sulfonato ligands (**A**) are by far the most common, and basically all examples of boron sulfonates [8,9,11,13] exhibit terminal sulfonato groups.

Only one example of a chelating bidentate coordination mode of a sulfonato group (η^2) is known (**B**) [14].

---

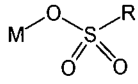
* Corresponding author. Tel.: +49-341-9736151; fax: +49-341-9604600.

E-mail address: hey@rz.uni-leipzig.de (E. Hey-Hawkins)

PII: S0022-328X(99)00204-1

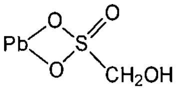
While no crystal structures of molecular compounds with bridging sulfonato groups (μ_2, **C**) have been reported, two-dimensional chains of metal atoms linked by bridging sulfonato groups are mainly known for Cu and Ag (12 compounds), Pb (two compounds) and seven other transition metals [15,16].

Only five compounds are known in which a sulfonato group acts as a triply bridging ligand (μ_3, **D**) and generates three-dimensional networks, four of which contain Cu or Ag [17,18].



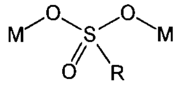
η^1, R = CF_3, alkyl, aryl, OH

A



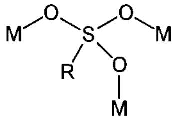
η^2

B



μ_2, R = CF_3, alkyl, aryl

C



μ_3, R = CF_3, alkyl

D

The small number of known disulfonato compounds all have two terminal (η^1) sulfonato ligands (**A**), which exhibit weak intermolecular interactions with other metal atoms [19,20]. As will be shown below, **2a–b** are the first compounds which exhibit two different bonding modes of sulfonato groups: terminal (**A**) and bridging (**C**).

2. Results and discussion

2.1. Synthesis and properties of *1a–c* and *2a–b*

Heating R_3B (R = Et, Bu, Pr^i) with equimolar amounts of $MeSO_3H$ in toluene for several hours gave, after work-up, a yellowish liquid, which was distilled in vacuo to give $R_2B(OSO_2Me)$ [R = Et (**1a**) [3a], Bu (**1b**), Pr^i (**1c**)] in 23–58% yield (Eq. (1)). In the case of Et_3B and Bu_3B, recrystallisation of the residual yellow or brown solid or oil from toluene gave $RB(OSO_2Me)_2$ [R = Et (**2a**), Bu (**2b**)] in 11–13% yield. The yield of **2a–b** can be increased by using two equivalents of methylsulfonic acid. As Pr^i_3B was less reactive, pivalic acid had to be added as catalyst [21], and no formation of the disulfonatoborane was observed. Compounds **1a–c** and **2a–b** are very soluble in toluene and even in pentane; they are extremely air sensitive. Compounds **1a–c** are pyrophoric, **2a–b** turn black on exposure to air almost instantaneously.

$$R_3B + n\,MeSO_3H \rightarrow R_{3-n}B(OSO_2Me)_n + n\,RH \qquad (1)$$

$n = 1$; R = Et (**1a**), Bu (**1b**), Pr^i (**1c**)
$n = 2$; R = Et (**2a**), Bu (**2b**)

Our attempts to prepare the corresponding Bu^t-substituted boron derivatives were thwarted by the fact that Bu^t_3B is unstable above 100°C and rearranges to give Bu^i_3B [22]. Compounds **1a** and **1b** were described previously by Trofimenko, but **1a** was only characterised by ^1H-NMR spectroscopy, and **1b** was only prepared in situ and not fully characterised [3].

The ^{11}B-NMR signals of the trialkylboranes R_3B (R = Et, Bu, Pr^i) are observed in the range 83–86 ppm, as expected [22]. The dialkyl(sulfonato)boranes **1a-c** exhibit singlets at 59.5 (**1a**), 59.2 (**1b**) and 58.4 ppm (**1c**), typical of three-coordinate boron compounds with one electron-withdrawing sulfonato group. Similar chemical shifts were observed for the related compounds $Cy_2B(OSO_2Me)$ (58.5 ppm) [5], (9-BBN)$B(OSO_2Me)$ (9-BBN = 9-borabicyclo[3.3.1]nonan, 58.2 ppm) [5], (*R*,*R*)-(MeCHCH$_2$CH$_2$CHMe)B(OSO$_2$Me) (62.2 ppm) [6] and the sulfate $Et_2B{-}OS(=O)_2O{-}BEt_2$ (61.0 ppm) [13]. For the disulfonato derivatives **2a–b**, the ^{11}B-NMR signal is observed at 27.7 (**2a**) and 26.0 ppm (**2b**), as expected for three-coordinate boron compounds with two electron-withdrawing sulfonato groups (cf. 33.0 ppm for $(EtB)_2(\mu\text{-}O)(\mu\text{-}SO_4)$ [13] and 30.4 ppm for $B_2(NMe_2)_2(tosylate)_2$ [9]). Accordingly, only one signal is observed for the methyl protons of the equivalent methylsulfonato groups at 2.22 (**2a**) and 2.33 ppm (**2b**). Apparently, at room temperature the dimeric arrangement observed for **2a** and **2b** in the solid state (vide infra) is not retained in solution. However, both compounds are dynamic in solution as this signal starts to coalesce at ca. 200 K (temperature limit in toluene-d_8).

In the ^{13}C-NMR spectra, the B–*C* groups are observed as a broad signal (due to the quadrupole moment of boron) at 8–23 ppm for the dialkyl(sulfonato)boranes [14.4 (**1a**), 22.7 (**1b**) and 18.0 ppm (**1c**)] and the alkyldi(sulfonato)boranes [8.7 (**2a**), 17.4 (**2b**)].

In the IR spectrum, the C–H stretching bands of **1a–c** and **2a–b** are observed in the expected range of 3100–2800 cm^{-1} (ν CH) and 1470–1370 cm^{-1} (δ CH) [23]. As most of the bands of **1a–c** and **2a–b** overlap with each other, unambiguous assignment is rarely possible. In **1a–c**, **2a–b** and related compounds, the B–O bands appear at 1315–1350 cm^{-1} [cf. 1329 in $MeB(OBu^t)_2$; 1346 in $Me_2B(OBu^t)$; 1347 cm^{-1} in $B(OBu^t)_3$] [24]. These absorptions overlap with those corresponding to ν_{as} O=S=O (1350–1310 cm^{-1} [23]). The C–S vibrations of methylsulfonates generally give rise to a strong absorption at 770–800 cm^{-1} (cf. 798 cm^{-1} in $\{Me_2Al(\mu\text{-}O_3SMe)\}_3$ [25], and 791, 788, and 778 cm^{-1} in $Na(SO_3Me)$ [26]). Characteristic bands for the terminal sulfonato groups $B{-}O{-}S(=O)_2Me$ of **1a–c** and **2a–b** were tentatively assigned by comparison with $Na(SO_3Me)$ [26] as follows: ν_{as} O=S=O: 1319 vs (**1a**), 1338 vs (**1b**), 1318 vs (**1c**), 1323 vs (**2a**), 1319 vs (**2b**); ν_s O=S=O: 1171 s (**1a**), 1183 s (**1b**), 1173 s (**1c**), 1182 vs (**2a**), 1180 vs (**2b**). By comparison with $\{Me_2Al(\mu O_3SMe)\}_3$ [25], in which the terminal S=O group is observed at 1308 cm^{-1} (vs) and the bridging O_2S group exhibits two bands at 1065 (ν_s SO_2, vs) and 1150 (ν_{as} SO_2, vs), the corresponding vibrations for the bridging sulfonato groups in **2a–b**, B–O–S(=O)Me–O–B, are tentatively assigned to the strong bands at 1129 (**2a**) or 1130 cm^{-1} (**2b**) (ν_{as} SO_2) and 970 (**2a**) or 987 cm^{-1} (**2b**) (ν_s SO_2).

For monoalkyl boranes with two electron-withdrawing groups, the B–C stretching vibration occurs around 1070 cm^{-1} ($MeBCl_2$ 1078, $MeBBr_2$ 1060 cm^{-1}), while for dialkyl derivatives, two bands are observed at 1080 and 1130 cm^{-1} (Me_2BCl 1080, 1120; Me_2BSH 1085, 1136 cm^{-1}) [27]. Again, these vibrations can not be unambiguously assigned in **1a–c** and **2a–b**, as they overlap with those of the methylsulfonato group.

2.2. Molecular structures of 1a, 2a and 2b

Although **1a** is liquid at ambient temperature, its melting point is 5–7°C, and we were able to grow crystals suitable for a crystal structure determination from a concentrated pentane solution at −30°C. The colourless crystals were isolated and kept below −30°C at all times to prevent melting. Colourless crystals of **2a** and **2b** were obtained from toluene at −30°C.

Compound **1a** crystallises in the monoclinic space group $P2_1/c$ (Fig. 1), **2a** in the triclinic space group $P\overline{1}$ (Fig. 2), and **2b** in the monoclinic space group $P2_1/n$ (Fig. 3). Selected bond lengths and angles are given in Tables 1–3.

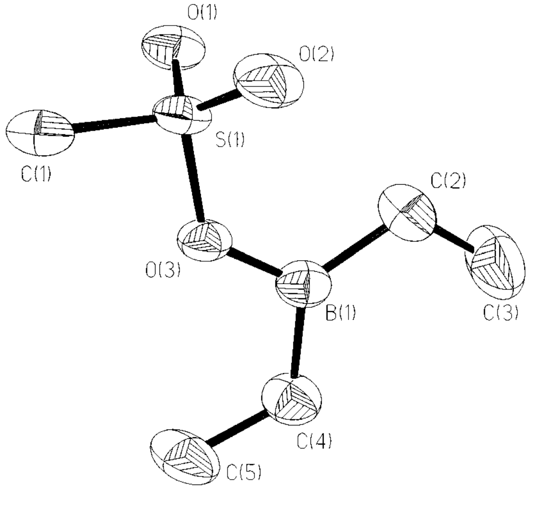


Fig. 1. Molecular structure of **1a** (ORTEP, 50% probability, SHELXTL PLUS; XP) [42]. Hydrogen atoms are omitted for clarity.

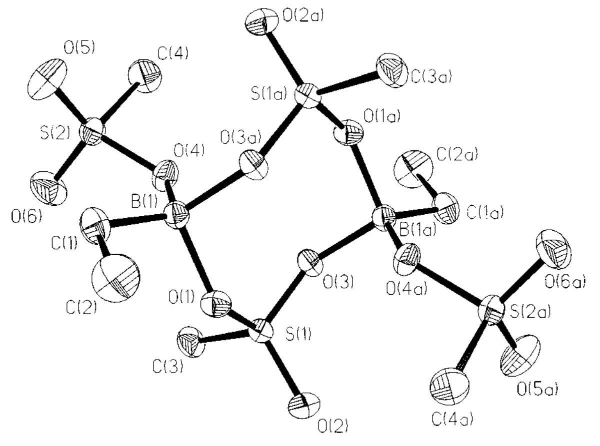


Fig. 2. Molecular structure of **2a** (ORTEP, 50% probability, SHELXTL PLUS; XP) [42]. Hydrogen atoms are omitted for clarity.

Interestingly, $Et_2B(OSO_2Me)$ (**1a**) is monomeric even in the solid state, whereas $EtB(OSO_2Me)_2$ (**2a**) and $BuB(OSO_2Me)_2$ (**2b**) are dimeric in the solid state with central $B_2O_4S_2$ eight-membered rings in which the centre of the eight-membered rings coincide with a crystallographic centre of inversion.

The boron atom in **1a** is coordinated in a distorted trigonal planar fashion [bond angles at B(1): O(3)–B(1)–C(4) 113.9(2), O(3)–B(1)–C(2) 120.8(2), C(4)–B(1)–C(2) 125.2(2)°] by two ethyl groups and a monodentate methylsulfonate ligand. The C–B–C bond angle is widened due to steric interaction of the ethyl groups.

In **2a** and **2b**, each boron atom is coordinated in a distorted tetrahedral fashion by one alkyl group, one monodentate sulfonato group and two oxygen atoms of two bridging sulfonato ligands. The O_t–B–C bond angles are widened to 121.2(2) (**2a**) and 118.2(2)° (**2b**), O_{br}–B–C to 109.3(2), 109.6(1)° for **2a** and to 107.6(2), 112.9(2)° for **2b**. The greater steric demand of the Bu group in **2b** compared to the Et group in

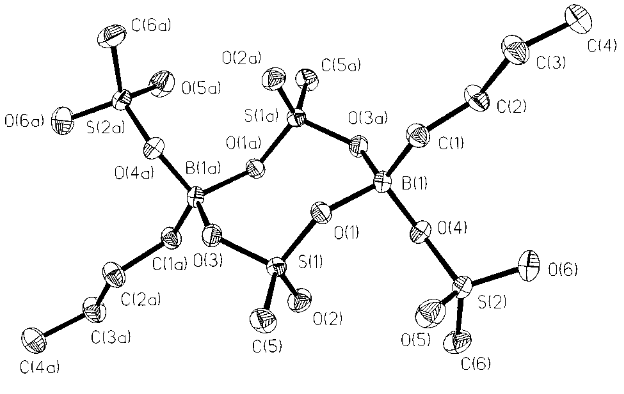


Fig. 3. Molecular structure of **2b** (ORTEP, 50% probability, SHELXTL PLUS; XP) [42]. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) in **1a**

Bond lengths (Å)			
S(1)–O(2)	1.427(2)	S(1)–O(1)	1.430(2)
S(1)–O(3)	1.578(1)	S(1)–C(1)	1.745(2)
O(3)–B(1)	1.412(3)	B(1)–C(4)	1.556(3)
B(1)–C(2)	1.563(4)	C(2)–C(3)	1.515(5)
C(4)–C(5)	1.521(4)		
Bond angles (°)			
O(2)–S(1)–O(1)	117.4(1)	O(2)–S(1)–O(3)	110.15(9)
O(1)–S(1)–O(3)	108.43(9)	O(2)–S(1)–C(1)	109.8(1)
O(1)–S(1)–C(1)	110.2(1)	O(3)–S(1)–C(1)	99.3(1)
B(1)–O(3)–S(1)	127.7(1)	O(3)–B(1)–C(4)	113.9(2)
O(3)–B(1)–C(2)	120.8(2)	C(4)–B(1)–C(2)	125.2(2)
C(3)–C(2)–B(1)	116.6(2)	C(5)–C(4)–B(1)	117.8(2)

2a results in a more pronounced distortion of the tetrahedral environment of B(1) in **2b**. Thus, the O_t–B–O_{br} bond angles in **2a** are 106.1(1) and 106.6(1)°, while for **2b** these angles differ by about 10° [O(4)–B(1)–O(1) 110.5(2), O(4)–B(1)–O(3a) 100.6(2)°]. The O_{br}–B–O_{br} bond angle is smaller in **2a** [102.5(1)°] and 106.5(2)° in **2b**.

The B–C bond lengths in **1a** [B(1)–C(4) 1.556(3), B(1)–C(2) 1.563(4) Å], **2a** [C(1)–B(1) 1.572(3) Å] and **2b** [B(1)–C(1) 1.581(3) Å] are in the range observed for alkylboranes (1.55–1.60 Å) [1b,10,28]. The B–O bond length of the monodentate sulfonato group in **1a** [B(1)–O(3) 1.412(3) Å] lies in the range expected for three-coordinate boron compounds (e.g. B–O 1.433(4) Å in *nido*-6-CF_3SO_3–$B_{10}H_{13}$ [8], B–O 1.436(4) Å in $B_2(NMe_2)_2(tosylate)_2$ [9], B–O(–S) 1.408(3), 1.426(3) Å in $(EtB)_2(\mu\text{-}O)(\mu\text{-}SO_4)$ [13]). As expected for four-coordinate boron compounds (e.g. B–O 1.54(4) Å in Cy_3P–$BH_2(OSO_2CF_3)$ [11], B–O 1.500(6), 1.506(6) Å in Cy_3P–$BH(OSO_2CF_3)_2$ [11]), the B–O bond lengths of the monodentate sulfonato groups in **2a** [O(4)–B(1) 1.466(2) Å] and **2b** [O(4)–B(1) 1.476(3) Å] are about 0.05–0.06 Å longer than those of **1a**, but about 0.07–0.09 Å shorter than those of the bridging sulfonato groups in **2a** [O(1)–B(1) 1.545(2), O(3)–B(1a) 1.557(2) Å] and **2b** [O(1)–B(1) 1.559(3), B(1)–O(3a) 1.548(3) Å]. In **1a**, **2a**, **2b** and related sulfonatoborane derivatives [9,13], the B–O–S bond angle of the monodentate and bidentate sulfonato groups are much larger than expected for sp^3 hybridisation [**1a**: B(1)–O(3)–S(1) 127.7(1)°; **2a**: B(1)–O(4)–S(2) 131.3(1), S(1)–O(1)–B(1) 130.6(1), S(1)–O(3)–B(1a) 128.9(1)°; **2b**: B(1)–O(4)–S(2) 125.5(1), S(1)–O(1)–B(1) 133.6(1), S(1)–O(3)–B(1a) 125.9(1)°], and this suggests p_π–p_π (O–B) and p_π–d_π (O–S) interactions.

Table 2
Selected bond lengths (Å) and angles (°) in **2a**

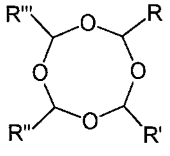
Bond lengths (Å)			
S(1)–O(2)	1.424(1)	S(1)–O(3)	1.504(1)
S(1)–O(1)	1.513(1)	S(1)–C(3)	1.742(2)
S(2)–O(5)	1.424(2)	S(2)–O(6)	1.429(2)
S(2)–O(4)	1.557(1)	S(2)–C(4)	1.750(2)
O(1)–B(1)	1.545(2)	O(3)–B(1a)	1.557(2)
O(4)–B(1)	1.466(2)	B(1)–O(3a)	1.557(2)
C(1)–C(2)	1.529(3)	C(1)–B(1)	1.572(3)
Bond angles (°)			
O(2)–S(1)–O(3)	114.76(8)	O(2)–S(1)–O(1)	109.47(8)
O(3)–S(1)–O(1)	109.38(8)	O(2)–S(1)–C(3)	111.2(1)
O(3)–S(1)–C(3)	103.70(9)	O(1)–S(1)–C(3)	108.00(9)
O(5)–S(2)–O(6)	117.5(1)	O(5)–S(2)–O(4)	111.00(9)
O(6)–S(2)–O(4)	108.04(9)	O(5)–S(2)–C(4)	110.0(1)
O(6)–S(2)–C(4)	109.3(1)	O(4)–S(2)–C(4)	99.4(1)
S(1)–O(1)–B(1)	130.6(1)	S(1)–O(3)–B(1a)	128.9(1)
B(1)–O(4)–S(2)	131.3(1)	C(2)–C(1)–B(1)	114.5(2)
O(4)–B(1)–O(1)	106.1(1)	O(4)–B(1)–O(3a)	106.6(1)
O(1)–B(1)–O(3a)	102.5(1)	O(4)–B(1)–C(1)	121.2(2)
O(1)–B(1)–C(1)	109.3(2)	O(3a)–B(1)–C(1)	109.6(1)

Table 3
Selected bond lengths (Å) and angles (°) in **2b**

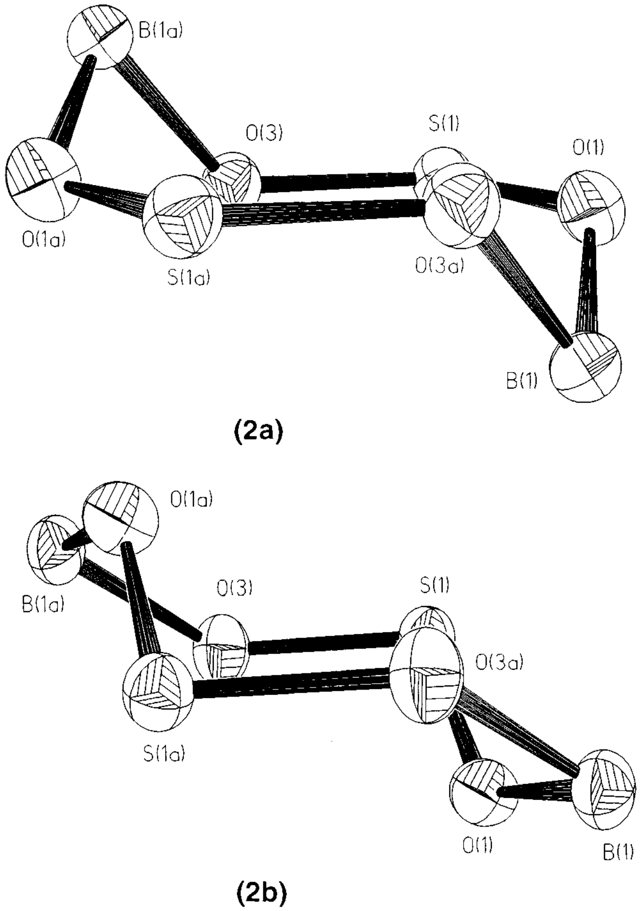
Bond lengths (Å)			
S(1)–O(2)	1.427(2)	S(1)–O(1)	1.514(2)
S(1)–O(3)	1.515(2)	S(2)–O(4)	1.557(2)
S(2)–O(6)	1.437(2)	S(2)–O(5)	1.437(2)
S(1)–C(5)	1.749(2)	S(2)–C(6)	1.759(3)
O(1)–B(1)	1.559(3)	O(3)–B(1a)	1.548(3)
O(4)–B(1)	1.476(3)	B(1)–O(3a)	1.548(3)
B(1)–C(1)	1.581(3)	C(1)–C(2)	1.540(3)
C(2)–C(3)	1.534(3)	C(3)–C(4)	1.532(3)
Bond angles (°)			
O(2)–S(1)–O(1)	114.73(9)	O(2)–S(1)–O(3)	114.44(9)
O(1)–S(1)–O(3)	105.97(9)	O(2)–S(1)–C(5)	113.0(1)
O(1)–S(1)–C(5)	104.4(1)	O(3)–S(1)–C(5)	103.1(1)
O(6)–S(2)–O(5)	117.2(1)	O(6)–S(2)–O(4)	109.4(1)
O(5)–S(2)–O(4)	110.1(1)	O(6)–S(2)–C(6)	108.9(1)
O(5)–S(2)–C(6)	110.0(1)	O(4)–S(2)–C(6)	100.0(1)
S(1)–O(1)–B(1)	133.6(1)	S(1)–O(3)–B(1a)	125.9(1)
B(1)–O(4)–S(2)	125.5(1)	O(4)–B(1)–O(3a)	100.6(2)
O(4)–B(1)–O(1)	110.5(2)	O(3a)–B(1)–O(1)	106.5(2)
O(4)–B(1)–C(1)	118.2(2)	O(3a)–B(1)–C(1)	112.9(2)
O(1)–B(1)–C(1)	107.6(2)	C(2)–C(1)–B(1)	114.7(2)
C(3)–C(2)–C(1)	113.4(2)	C(2)–C(3)–C(4)	113.0(2)

The S–O(–B) bond lengths of the monodentate sulfonate groups in **1a** [S(1)–O(3) 1.578(1) Å], **2a** [S(2)–O(4) 1.557(1) Å] and **2b** [S(2)–O(4) 1.557(2) Å] are comparable to those of related B–OS(=O)$_2$R derivatives [8,9]. The terminal S–O bonds of the sulfonato ligands in **1a** [S(1)–O(2) 1.427(2), S(1)–O(1) 1.430(2) Å], **2a** [S(2)–O(5) 1.424(2), S(2)–O(6) 1.429(2) Å] and **2b** [S(2)–O(5) 1.437(2), S(2)–O(6) 1.437(2) Å] and related sulfonatoborane derivatives [8,9] are ca. 0.15 Å shorter and resemble double bonds. The S–C bond lengths are as expected [**1a**: S(1)–C(1) 1.745(2); **2a**: S(1)–C(3) 1.742(2), S(2)–C(4) 1.750(2); **2b**: S(1)–C(5) 1.749(2), S(2)–C(6) 1.759(3) Å]. The O=S=O bond angle of the monodentate sulfonato group is large [**1a**: O(2)–S(1)–O(1) 117.4(1); **2a**: O(5)–S(2)–O(6) 117.5(1); **2b**: O(5)–S(2)–O(6) 117.2(1)°], and the (B–)O–S–C bond angle small [**1a**: O(3)–S(1)–C(1) 99.3(1); **2a**: O(4)–S(2)–C(4) 99.4(1); **2b**: O(4)–S(2)–C(6) 100.0(1)°], while the other bond angles lie in the range of 108–111° expected for a tetrahedral environment.

The central $B_2O_4S_2$ units of **2a** and **2b** have a chair conformation (Fig. 4), which is uncommon for eight-membered rings. Other examples of inorganic compounds include S_4N_4 (cage structure) and $(NPCl_2)_4$ (boat conformation) [29]. Elemental sulfur and selenium (S_8, Se_8) [29], as well as most 1,3,5,7-substituted organic eight-membered rings [30], which include 2,4,6,8-substituted 1,3,5,7-tetraoxocanes (**E**) such as metaldehyde [31], adopt a crown conformation. Exceptions are 1,3,5,7-tetrathiocane (boat-chair conformation) [31], metachloral (chair conformation) [31] and 1,2,5,6-tetrabromocyclooctane (twist-chair conformation) [32].



E



(2a)

(2b)

Fig. 4. Central eight-membered $B_2O_4S_2$ rings in **2a** and **2b** showing the chair conformation (SHELXTL PLUS; XP) [42].

3. Conclusions

For the first time, alkylboron sulfonates have been structurally characterised. While the monoalkyl(sulfonato)borane **1a** is monomeric even in the solid state, the dialkyl(sulfonato)boranes **2a** and **2b** are dimeric and exhibit two different types of sulfonato substituents: terminal and bridging. We are now investigating the synthetic potential of these compounds in transition metal chemistry.

4. Experimental

All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. The NMR spectra were recorded at 25°C in C_6D_6 with an AVANCE DRX 400 spectrometer (Bruker), ^{1}H-NMR: internal standard solvent (benzene), external standard TMS; ^{13}C-NMR: external standard TMS, internal standard solvent; ^{11}B-NMR: external standard $BF_3 \cdot Et_2O$. The IR spectra were recorded on a FT-IR spectrometer Perkin–Elmer System 2000 in the range 350–4000 cm^{-1}. X-ray structural analyses: Siemens SMART CCD diffractometer. The melting points were determined in sealed capillaries under argon and are uncorrected. Complex **1a** was prepared as described earlier [3a]. Bu_3B [33] and Pr^i_3B [34] were prepared according to the literature procedure from $BF_3 \cdot Et_2O$ and the corresponding Grignard reagent. Et_3B and $MeSO_3H$ are commercially available (Aldrich).

The NMR data of the trialkylboranes have been published before. As each paper refers to the NMR study of one nucleus only (BEt_3: ^{11}B [35], ^{1}H [36]; Bu_3B: ^{11}B [37], ^{1}H [38]; and Pr^i_3B: ^{11}B [39], ^{13}C [40]; ^{1}H [41]), we have repeated the NMR spectroscopic investigations, and the chemical shifts and coupling constants are given below.

Triethylborane, *Et₃B* (*NMR data for comparison*): ^{1}H-NMR (400.1 MHz): $\delta = 0.95$ (t, 9H, CH_2CH_3, $^3J_{H-H}$: 7.2 Hz), 1.11 (q, 6H, B–CH_2, $^3J_{H-H}$: 7.2 Hz). ^{11}B-NMR (128.4 MHz): $\delta = 86.0$, s. ^{13}C-NMR (100.6 MHz): $\delta = 8.93$ (CH_2CH_3), 20.32 (br, B–C).

Tri-n-butylborane, *Bu_3B*: b.p. 40°C at 5×10^{-2} torr. *NMR data for comparison:* ^{1}H-NMR (400.1 MHz): $\delta = 0.95$ (t, 3H, CH_2CH_3, $^3J_{H-H}$: 7.2 Hz), 1.22 (t, 2H, B–CH_2), 1.33–1.43 (m, 4H, CH_2–CH_2). ^{11}B-NMR (128.4 MHz): $\delta = 85.8$, s. ^{13}C-NMR (100.6 MHz): $\delta = 14.99$ (CH_2CH_3), 27.06 (CH_2), 27.84 (CH_2), 29.01 (br, B–C).

Tri-i-propylborane, Pr^i_3B: Pr^i_3B was prepared by a modified procedure for Ph_3B [33]. As Pr^i_3B (b.p. 45°C at 25 torr) is not easily separated from the solvent (toluene), the synthesis was modified and carried out in Et_2O. *NMR data for comparison*: ^1H-NMR (400.1 MHz): $\delta = 0.92$ (d, 6H, $CH(C\mathit{H}_3)_2$, $^3J_{H-H}$: 7.2 Hz), 1.65 (sept, 1H, $C\mathit{H}(CH_3)_2$, $^3J_{H-H}$: 7.2 Hz). ^{11}B-NMR (128.4 MHz): $\delta = 83.7$.

General procedure for the preparation of $R_2B(OSO_2Me)$ [R = Et (**1a**) [3a], Bu (**1b**)] and $RB(OSO_2Me)_2$ [R = Et (**2a**), Bu (**2b**)]: In a flask fitted with a reflux condenser and a bubbler, freshly dried methylsulfonic acid was dissolved in 200 ml toluene, and trialkylboron was added. The mixture was refluxed for several hours until gas evolution stopped. The toluene was removed in vacuo, and the remaining slightly yellow liquid distilled in vacuo to give **1a–b**. A yellow solid (R = Et) or brown oil (R = Bu) remained in the flask. It was recrystallised from toluene to yield **2a–b**.

1a, **2a**: 22.2 g (15 ml, 0.23 mol) $MeSO_3H$, 25.6 g (39 ml, 0.27 mol) Et_3B, yield: **1a**: 23.0 g (61%), colourless liquid, b.p.: 56–58°C at 0.2 torr, m.p. 5–7°C; **2a**: 6.6 g (13%), colourless solid, m.p. (dec.) 78–80°C.

1b, **2b**: 15.8 g (0.16 mol) $MeSO_3H$, 30.0 g (0.16 mol) Bu_3B, yield: **1b**: 30.0 g (58%), colourless liquid, b.p.: 60°C at 5×10^{-2} torr, does not solidify down to -15°C; **2b**: 4.3 g (11%), colourless solid, m.p. 56°C.

1a: ^1H-NMR (400.1 MHz): $\delta = 0.79$ (t, 6H, $CH_2C\mathit{H}_3$, $^3J_{H-H}$: 7.6 Hz), 1.05 (q, 4H, $B-C\mathit{H}_2$, $^3J_{H-H}$: 7.6 Hz), 2.35 (s, 3H, $S-C\mathit{H}_3$). ^{11}B-NMR (128.4 MHz): $\delta = 59.5$. ^{13}C-NMR (100.6 MHz): $\delta = 7.89$ ($CH_2\mathit{C}H_3$), 14.4 (br, $B-\mathit{C}H_2$), 39.71 ($S-\mathit{C}H_3$). IR (KBr), ν (cm^{-1}) = 3027 m, 2962 m–s, 2935 m, 2873 m, 1462 m, 1415 m, 1319 vs, 1171 vs, 1129 s, 971 s, 931 vs, 820 s, 757 s.

2a: ^1H-NMR (400.1 MHz): $\delta = 0.82$ (br, t, 3H, $CH_2C\mathit{H}_3$), 1.13 (br, 2H, $B-C\mathit{H}_2$), 2.22 (s, 6H, $S-C\mathit{H}_3$). ^{11}B-NMR (128.4 MHz): $\delta = 27.7$. ^{13}C-NMR (100.6 MHz): $\delta = 7.12$ ($CH_2\mathit{C}H_3$), 8.7 (br, $B-\mathit{C}H_2$), 39.44 ($S-\mathit{C}H_3$). IR (KBr), ν (cm^{-1}) = 3044 s, 3029 s, 2946 s, 2878 m, 1465 m, 1420 m, 1323 vs, 1182 vs, 1129 s, 970 s, 924 vs, 848 s, 805 s, 778 s.

1b: ^1H-NMR (400.1 MHz): $\delta = 0.86$ (t, 6H, $CH_2C\mathit{H}_3$, $^3J_{H-H}$: 7.0 Hz), 1.14 (t, 4H, $B-C\mathit{H}_2$), 1.26 (m, 8H, $C\mathit{H}_2-C\mathit{H}_2$), 2.28 (s, 3H, $S-C\mathit{H}_3$). ^{11}B-NMR (128.4 MHz): $\delta = 59.2$, s. ^{13}C-NMR (100.6 MHz): $\delta = 14.77$ ($CH_2\mathit{C}H_3$), 22.7 (br, $B-\mathit{C}H_2$), 26.42 ($\mathit{C}H_2$), 26.61 ($\mathit{C}H_2$), 39.75 ($S-\mathit{C}H_3$). IR (KBr), ν (cm^{-1}) = 3026 w, 2958 s, 2931 s, 2874 s, 1460 m, 1415 sh, 1338 vs, 1183 s, 1075 s, 972 s, 908 s, 840 m, 783 m.

2b: ^1H-NMR (400.1 MHz): $\delta = 0.84$ (t, 3H, $CH_2C\mathit{H}_3$, $^3J_{H-H}$: 7.2 Hz), 1.24 (m, 4H, $C\mathit{H}_2-C\mathit{H}_2$), 1.40 (m, 2H, $C\mathit{H}_2$), 2.33 (s, 6H, $S-C\mathit{H}_3$). ^{11}B-NMR (128.4 MHz): $\delta = 26.0$, s. ^{13}C-NMR (100.6 MHz): $\delta = 14.62$ ($CH_2\mathit{C}H_3$), 17.4 (br, $B-\mathit{C}H_2$), 26.06 (2C, shown by 2D-experiment, $\mathit{C}H_2-\mathit{C}H_2$), 39.87 ($S-\mathit{C}H_3$). IR (KBr), ν (cm^{-1}) = 3026 m, 2957 m, 2932 s, 2856 m, 1465 m, 1418 m, 1319 vs, 1180 vs, 1130 s, 987 vs, 920 vs, 830 s, 761 s.

$Pr^i_2B(OSO_2Me)$ (**1c**): In a flask fitted with a reflux condenser and a bubbler, freshly dried methylsulfonic acid (7.9 g, 0.08 mol) was dissolved in 200 ml toluene, and 11.2 g (0.08 mol) Pr^i_3B was added. As Pr^i_3B is less reactive as Et_3B and Bu_3B, pivalic acid [21] (0.05 g, 0.5 mmol) was added as a catalyst. The mixture was refluxed for 15 h. The toluene was removed in vacuo, and the remaining slightly yellow liquid distilled in vacuo to give **1c**. Yield: 3.5 g (23%), b.p. 42°C at 10^{-2} torr.

^1H-NMR (400.1 MHz): $\delta = 0.90$ (d, 12H, $CH(C\mathit{H}_3)_2$, $^3J_{H-H}$: 7.2 Hz), 1.68 (m, 2H, $C\mathit{H}(CH_3)_2$), 2.35 (s, 3H, $S-C\mathit{H}_3$). ^{11}B-NMR (128.4 MHz): $\delta = 58.4$. ^{13}C-NMR (100.6 MHz): $\delta = 17.82$ ($CH(\mathit{C}H_3)_2$), 18.0 (br, $\mathit{C}H(CH_3)_2$), 39.74 ($S-\mathit{C}H_3$). IR (KBr), ν (cm^{-1}) = 3032 w, 2955 m, 2892 sh, 2871 m, 1469 m, 1414 m, 1318 vs, 1173 s, 1136 m, 968 s, 939 s, 836 m, 763 m.

X-ray crystal structure determination for **1a, 2a** and **2b** (see Section 5): data ($Mo-K_\alpha = 0.71073$ Å) were collected with a Siemens CCD (SMART). All observed reflections were used for determination of the unit cell parameters. The structure was solved by direct methods (SHELXTL PLUS [42]) and subsequent difference Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL PLUS [42]). B, S, O, and C atoms anisotropic, H atoms located and refined isotropically. Empirical absorption correction with SADABS [43]. Crystals of **1a** were isolated and kept below -30°C at all times to prevent melting, using a modified procedure described by Bärnighausen et al. [44].

Crystal data for **1a**: $C_5H_{13}BO_3S$, $M = 164.02$, white crystals, $0.40 \times 0.30 \times 0.10$ mm, monoclinic, space group $P2_1/c$ (no. 14), $T = 213(2)$ K, $a = 12.905(1)$, $b = 8.111(1)$, $c = 8.938(1)$ Å, $\beta = 104.63(1)°$, $V = 905.30(2)$ Å^3, $Z = 4$, $D_c = 1.504$ Mg m^{-3}, $F(000) = 440$, $\mu(Mo-K_\alpha) = 0.388$ mm^{-1}, 7068 reflections collected with $1.6° < \theta < 27.7°$; of these, 1987 were independent; 143 parameters, refinements converge to $R_1 = 0.0452$, $wR_2 = 0.1341$ (for reflections with $I > 2\sigma(I)$), $R_1 = 0.0550$, $wR_2 = 0.1468$ (all data). Crystal data for **2a***:* $C_8H_{22}B_2O_{12}S_4$, $M = 460.12$, white crystals, $0.30 \times 0.20 \times 0.20$ mm, triclinic, space group $P\bar{1}$ (no. 2), $T = 213(2)$ K, $a = 7.820(2)$, $b = 8.124(2)$, $c = 8.644(2)$ Å, $\alpha = 86.78(3)$, $\beta = 80.35(3)$, $\gamma = 63.17(3)°$, $V = 482.9(2)$ Å^3, $Z = 1$, $D_c = 1.582$ Mg m^{-3}, $F(000) = 240$, $\mu(Mo-K_\alpha) = 0.546$ mm^{-1}, 2584 reflections collected with $2.4° < \theta < 27.1°$; of these, 1840 were independent; 162 parameters, refinements converge to $R_1 = 0.0372$, $wR_2 = 0.1046$ (for reflections with $I > 2\sigma(I)$), $R_1 = 0.0381$, $wR_2 = 0.1063$ (all data). Crystal data for **2b***:* $C_{12}H_{30}B_2O_{12}S_4$, $M = 516.22$, white crystals, $0.50 \times 0.40 \times 0.30$ mm, monoclinic, space group $P2_1/n$ (no. 14), $T = 205(2)$ K, $a = 10.273(1)$, $b = 8.629(1)$, $c = 13.292(1)$ Å, $\beta = 90.99(1)$, $V = 1178.02(5)$ Å^3, $Z = 2$, $D_c = 1.455$ Mg m^{-3}, $F(000) = 544$, $\mu(Mo-K_\alpha) = 0.456$ mm^{-1}, 6437 reflections collected with $2.5° < \theta < 27.8°$;

of these, 2527 were independent; 196 parameters, refinements converge to $R_1 = 0.0390$, $wR_2 = 0.1048$ (for reflections with $I > 2\sigma(I)$), $R_1 = 0.0426$, $wR_2 = 0.1087$ (all data).

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (**1a**: CCDC 115524, **2a**: CCDC 115523, **2b**: CCDC 115525). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033, e-mail: teched@chemcrys.cam.ac.uk).

Acknowledgements

The authors gratefully acknowledge financial support from the Fonds der chemischen Industrie (Kekulé-Stipendium for R.P.), the Alexander von Humboldt Foundation (F.B.S.) and the Landesgraduiertenförderung (Sachsen) (scholarship for S.B.).

References

[1] (a) R. Schlengermann, J. Sieler, S. Jelonek, E. Hey-Hawkins, Chem. Commun. (1997) 197. (b) R. Schlengermann, J. Sieler, E. Hey-Hawkins, Main Group Chem. 2 (1997) 141.
[2] (a) H. Braunschweig, C. Kollmann, U. Englert, Angew. Chem. 110 (1998) 3355. (b) review: H. Braunschweig, Angew. Chem. 110 (1998) 1882. (c) review: G.J. Irvine, M.J.G. Lesley, T.B. Marder, N.C. Norman, C.R. Rice, E.G. Robins, W.R. Roper, G.R. Whittell, L.J. Wright, Chem. Rev. 98 (1998) 2685.
[3] (a) S. Trofimenko, J. Am. Chem. Soc. 91 (1969) 2139. (b) S. Trofimenko, Inorg. Chem. 8 (1969) 1714.
[4] J. Bielawski, K. Niedenzu, Inorg. Chem. 25 (1986) 85.
[5] H.C. Brown, K. Ganesan, R.K. Dhar, J. Org. Chem. 58 (1993) 147 (and Refs. therein).
[6] S. Masamune, R.M. Kennedy, K.N. Houk, Y. Wu, J. Am. Chem. Soc. 108 (1986) 7404.
[7] D.A. Evans, J.V. Nelson, E. Vogel, T.R. Taber, J. Am. Chem. Soc. 103 (1981) 3099.
[8] M.F. Hawthorne, I.J. Mavunkal, C.B. Knobler, J. Am. Chem. Soc. 114 (1992) 4427.
[9] H. Nöth, M. Wagner, Chem. Ber. 124 (1991) 1963.
[10] M. Müller, E. Eversheim, U. Englert, R. Boese, P. Paetzold, Chem. Ber. 128 (1995) 99.
[11] T. Imamoto, K. Asakura, H. Tsuruta, K. Kishikawa, K. Yamaguchi, Tetrahedron Lett. 37 (1996) 503.
[12] J. Charalambous, M.J. Frazer, W. Gerrard, J. Chem. Soc. (1963) 826.
[13] R. Köster, W. Schüßler, D. Bläser, R. Boese, Chem. Ber. 127 (1994) 1593.
[14] S. Larsen, F.M. Nicolaisen, A.M. Schønemann, Acta Chem. Scand. 46 (1992) 1135.
[15] R. Guilard, P. Cocolios, P. Fournari, C. Lecomte, J. Protas, J. Organomet. Chem. 168 (1979) C49.
[16] M. Veith, B.W. Royan, V. Huch, Phosphorus, Sulfur and Silicon 79 (1993) 25.
[17] P.J.J.A. Timmermans, A. Mackor, A.L. Spek, B. Kojic, J. Organomet. Chem. 276 (1984) 287.
[18] G. Smith, D.E. Lynch, C.H.L. Kennard, Inorg. Chem. 35 (1996) 2711.
[19] R. Ruether, F. Huber, H. Preut, Z. Anorg. Allg. Chem. 539 (1986) 110.
[20] F. Huber, J. Remer, M. Schuermann, Acta Crystallogr. C50 (1994) 1913.
[21] R. Köster, W. Fenzl, G. Seidel, Liebigs Ann. Chem. (1975) 352.
[22] H. Nöth, T. Taeger, J. Organomet. Chem. 142 (1977) 281.
[23] M. Hesse, H. Meier, B. Zeeh, Spektroskopische Methoden in der Organischen Chemie, 5. Auflage, Georg Thieme Verlag, Stuttgart, 1995.
[24] J. Kronawitter, H. Nöth, Chem. Ber. 105 (1972) 2423.
[25] H. Olapinski, J. Weidlein, H.-D. Hausen, J. Organomet. Chem. 64 (1974) 193.
[26] W.K. Thompson, Spectrochim. Acta 28A (1972) 1479.
[27] J. Weidlein, U. Müller, K. Dehnicke, Schwingungsfrequenzen I, G. Thieme Verlag, Stuttgart, 1981.
[28] (a) A. Meller, H. Hoppe, W. Maringgle, A. Haase, M. Noltemeyer, Organometallics 17 (1998) 123. (b) H. Hommer, H. Nöth, J. Kizek, W. Ponikwar, H. Schwenk-Kircher, Eur. J. Inorg. Chem. (1998) 1519.
[29] A.F. Hollemann, E. Wiberg, Lehrbuch der Anorganischen Chemie, 101st edition, Walter de Gruyter, Berlin, 1995.
[30] F.A.L. Anet, P.J. Degen, J. Am. Chem. Soc. 94 (1972) 1390 (and Refs therein).
[31] D.G. Hay, M.F. Mackay, Aust. J. Chem. 33 (1980) 2249 (and Refs therein).
[32] G. Ferguson, D.D. MacNicol, W. Oberhansli, R.A. Raphael, J.A. Zabkiewicz, J. Chem. Soc., Chem. Commun. (1968) 103.
[33] J.R. Johnson, H.R. Snyder, M.G. van Campen, J. Am. Chem. Soc. 60 (1938) 115.
[34] E. Krause, P. Nobbe, Chem. Ber. 64 (1931) 2112.
[35] H. Nöth, H. Vahrenkamp, Chem. Ber. 99 (1966) 1049.
[36] E.G. Hoffmann, Z. Analyt. Chem. 70 (1959) 177.
[37] A.G. Davies, B.P. Roberts, J.C. Scaiano, J. Chem. Soc. Perkin Trans. 2 (1972) 803.
[38] M. Schmidt, F.R. Rittig, Z. Naturf. 25B (1970) 887.
[39] J. Kroner, B. Wrackmeyer, J. Chem. Soc. Faraday Trans. 2 72 (1976) 2283.
[40] F.J. Weigert, J.D. Roberts, Inorg. Chem. 12 (1973) 313.
[41] A.H. Cowley, T.A. Furtsch, J Am Chem. Soc. 91 (1969) 39.
[42] SHELXTL PLUS, Siemens Analyt. X-ray Inst. Inc., 1990, XS: Program for Crystal Structure Solution, XL: Program for Crystal Structure Determination, XP: Interactiv Molecular Graphics.
[43] G.M. Sheldrick, 1998, SADABS, a Program for Empirical Absorption Correction, Göttingen.
[44] M. Veith, H. Bärnighausen, Acta Crystallogr. 30 (1974) 1806.