enjoy distorted octahedral geometry through ligation to the bridging oxygen atoms of the methoxy groups, to the terminal nitrogen donors of the diazenido units, and to the bridging oxo groups of the molybdate units that span the $Mo_2(OCH_3)_2$ rhombus; the average bond distances are 2.140 (8), 1.823 (9), and 2.063 (8) Å, respectively. The Mo1-Mo3 distance of 3.465 Å is indicative of the absence of a significant metal-metal interaction within the $[Mo_2(OCH_3)_2(NNC_6H_5)_4]^{2+}$ moiety. Molybdenum-molybdenum distances for oxo-bridged units average 3.413 Å.

The short average Mo-N distance of 1.823 (9) Å, together with the average N-N distance of 1.227 (12) Å and the linearity of the Mo-N-N unit, is common to the molybdenum-diazenido grouping, indicating extensive delocalization throughout the unit and significant multiple-bond character to the Mo-N and N-N bonds. The electron count for this anion is consistent with the diazenido ligand behaving as a three-electron donor and consequently with the absence of a metal-metal bond, a feature consistent with the observed Mo1-Mo3 bond distance.

The structure is not related to the isopolymolybdate structures mentioned earlier where the molybdenum atoms are pseudooctahedrally coordinated Mo(VI) units. In the present case, the tetrahedral molybdate unit MoO_4^{2-} shares a vertex with each of the Mo1 and Mo3 octahedra, which in turn share an edge defined by the O11-O12 vector. The $[Mo(NNC_6H_5)_2]^{2+}$ unit appears to be a robust chemical unit that persists in the structural chemistry of molybdenum. The oxidation state of the molybdenum in this unit is somewhat ambiguous, as assignment of an average oxidation state of +3 to the molybdenum atoms of the diamagnetic anion is not particularly instructive. However, comparison of the metrical parameters for the metal-diazenido moiety of this structure with those of other examples of organodiazo complexes[12] confirms that the phenyldiazo grouping is best described as the three-electron-donating $-N_2R^+$ structure. Hence, the molybdenum oxidation state may be assigned, in a formal sense, as Mo(0).[13]

The complex anion is reactive toward both oxidation-reduction reactions and substitution reactions at the oxo centers, providing a useful synthetic precursor for a variety of complexes incorporating the $[Mo(NNC_6H_5)_2]^{2+}$ core. Reaction with arenethiolate ligands yields binuclear species $[Mo_2(NNAr)_4(SR)_5]^-$,[14] whereas reactions with sterically demanding thiolates such as 2,4,6-triisopropylthiophenol, TIPT, give monomeric species, $[Mo(NNC_6H_5)L(TIPT)_3]$ ($L = CH_3CN$).[15] With alcohols a variety of products may be isolated, the most remarkable of which is $[Mo_2Cl_2(OC_2H_5)_4(NNC_6H_5)_4]$, an ethoxy-bridged binuclear complex formed by C-C bond cleavage of butane-2,3-diol in CH_2Cl_2 solution[16]

Synthetic studies are in progress to exploit the synthetic potential of the tetranuclear precursor and to test the persistence of the *cis*-$[Mo(NNC_6H_5)_2]^{2+}$ unit, a moiety that appears to exhibit structural and chemical characteristics similar to those of the well-known *cis*-$[MoO_2]^{2+}$ unit, a characteristic feature of Mo(VI) chemistry.

Supplementary Material Available: Listings of atomic positional parameters, bond lengths, bond angles, anisotropic temperature factors, and hydrogen atom positions (8 pages). Ordering information is given on any current masthead page.

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(13) Reference 6 describes the structure of the complex $[Mo(NNC_6H_4OCH_3)_2L]$, previously assigned as a Mo(VI) species. Although the structure is somewhat poorly resolved, the parameters associated with the $[MoN_2R]$ unit are in fact more similar to those observed for hydrazido(2-) complexes, $[MoN_2HR]$, than to those associated with the molybdenum-diazenido moiety, $[MoN_2R]$. This raises some question as to the true identity of this complex and suggests that more accurate crystallographic data be obtained, in conjunction with spectroscopic studies of the molybdenum-nitrogen unit.

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Articles

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Solid-State ^{11}B NMR Studies on Boron-Chalcogenide Systems

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Solid-state ^{11}B NMR techniques are used to study the structural nature of various phases obtained in the systems boron-sulfur, boron-selenium, boron-sulfur-selenium, and boron-tellurium. It is demonstrated that the method can be used efficiently for the structural characterization of these hydrolytically sensitive and glass-forming systems. In the system B-S the novel compound BS_2 is observed at higher S:B ratios besides B_2S_3 at lower ones. In the system B-Se, BSe_2 rather than the expected B_2Se_3 is observed as the only product besides a subselenide with B-B bonds. All phases except the subselenide contain trigonally coordinated boron. No binary boron-tellurium compounds are detected. Quadrupole coupling constants of B_2S_3 (2.46 MHz), BS_2 (2.16 MHz), and BSe_2 (2.07 MHz) are determined and interpreted in terms of the bond properties.

Introduction

Investigation of non-oxide boron-chalcogenide chemistry in the solid state is hampered by severe experimental difficulties. High-temperature synthetic conditions are required that may involve considerable chemical attack of the different container materials by the reaction products. Moreover, the inherent tendency toward vitrification makes an X-ray characterization of these systems very difficult. Finally, the physicochemical investigation is severely restricted by the extreme sensitivity of the non-oxide boron chalcogenides toward hydrolysis. Owing to these unfavorable properties, the present state of the art appears rather diffuse. Although several studies have been undertaken, neither is there a clear picture of the existing compounds in the solid state nor are many of those published in the literature[2-15]

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Table I. Published Compositions of Solid Binary Boron Chalcogenides

S compn	ref	Se compn	ref	Te compn	ref
$B_{12}S$	2				
B_4S	3	B_4Se	10	no compd exists	5, 16
BS	4, 5	B_2Se	11		
B_2S_3	5–7, 9	B_2Se_3	5, 12–14		
BS_2	5, 6, 8[a]	BSe_2	15[a]		
B_2S_5	9				

[a] Reported only in the gas phase.

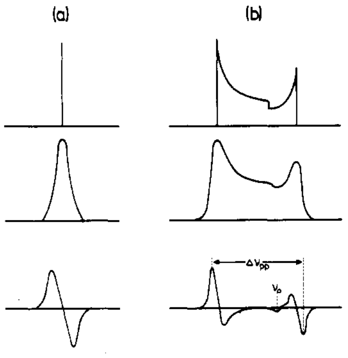

Figure 1. ^{11}B NMR powder patterns as expected in the absence (a) and presence (b) of second-order quadrupole interaction ($I = {}^3/_2$, $\eta = 0$). The upper trace represents the theoretical line shape, the middle trace results from the simultaneous presence of dipolar interactions, the bottom trace shows the first derivative, which is experimentally recorded.

(cf. Table I) well characterized. Finally, considerable uncertainty remains with respect to the experimental conditions that permit the synthesis of larger amounts of material. This situation is in contrast to detailed knowledge of the gas phase above boron–sulfur and boron–selenium systems obtained from mass spectra that show a number of monomeric and oligomeric species[8,15] derived from gaseous parent molecules $(B_2S_3)_n$ and $(BS_2)_n$ in the case of the sulfides.[8]

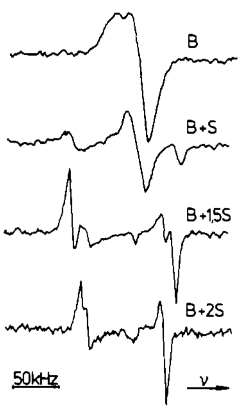

Figure 2. Variation of the ^{11}B NMR spectra in the system B–S as a function of composition.

In the present study a novel type of approach is made by using solid-state NMR as a structural and diagnostic tool. Owing to its inherent nature and capacity, NMR first of all provides information about the immediate surroundings of the nuclear probes within the material. With respect to the examination of systems that tend to form glasses this is an advantageous property since the spectral information remains basically unaffected by the lack of long-range order.[17] Furthermore, possible sources of error arising from sample hydrolysis and oxidation are eliminated because the experiment is noninvasive and can be conducted directly on the sealed reaction ampules. These advantages in addition to the fact that the ^{11}B nuclei respond very sensitively to changes in their chemical environment make NMR a valuable tool to monitor the synthesis, optimize its parameters, and identify the product distribution. Beyond these rather practical aspects interesting structure and bonding information can be obtained. Since ^{11}B nuclei possess an electric quadrupole moment probing the electric field gradient (EFG) at the nuclear site, valuable information about site symmetry and chemical bonding properties is available.[18] Thus, the quadrupole coupling vanishes in a regular tetrahedral environment (sp^3 hybridization), and the spectra are governed by dipolar coupling (Figure 1a). On the other hand, a planar triangular coordination (sp^2 hybridization) creates a large electric field gradient that causes second-order quadrupole splitting. In these cases spectra of the type of Figure 1b are observed, from which the principal quadrupole coupling constant e^2qQ/h and the asymmetry parameter of the EFG can be evaluated by computer fitting.[19] For regular D_{3h} site symmetry, $\eta = 0$ and the coupling constant can be directly extracted from the spectra according to the formula

$$\frac{e^2qQ}{h} = \frac{8}{5}I(2I-1)\left[\frac{\nu_0\Delta\nu_{pp}}{I(I+1)-\frac{3}{4}}\right]^{1/2}$$

where ν_0 and $\Delta\nu_{pp}$ are defined in Figure 1b. Since these values depend sensitively upon chemical bond properties, they provide useful spectroscopic fingerprint data for the identification of boron compounds.

Another valuable aspect of ^{11}B NMR arises from its relaxation behavior. As pointed out previously,[20] very effective quadrupolar relaxation modes, which appear to be intrinsic to the glass state, permit the application of high radiofrequency power levels in noncrystalline materials. In contrast these relaxation modes are absent in rigid crystalline solids. Thus, the observed saturation

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Table II. Composition, Experimental Conditions, and Characterization of the Samples Studied

compn	time (temp, °C)	descrpn	compds present acc to NMR
B + S	1 h (900)	glassy	B + B_2S_3
2 B + 3 S	0.5 h (850)	brown glassy (major) + yellow cryst (minor)	B_2S_3 + BS_2
2 B + 4 S	0.5 h (850)	yellow cryst	BS_2
2 B + 6 S	0.5 h (850)	yellow matl	BS_2 + S
4 B + Se	1 h (900)	brown, amorphous	B + subselenide
2 B + Se	1 h (900)	brown, amorphous	B + subselenide
B + Se	0.5 h (900)	amorphous yellow matl + red sublimable compd	BSe_2 + subselenide
	3 days (700)	amorphous yellow matl	subselenide
2 B + 3 Se	0.5 h (900)	amorphous yellow matl + red sublimable compd	BSe_2 + subselenide
2 B + 4 Se	0.5 h (900)	red, homogeneous prod	BSe_2
2 B + 4.5 Se	0.5 h (900)	red, amorphous	BSe_2-Se glass
	7 days (450)	red, amorphous	BSe_2-Se glass
2 B + 2 S + Se	1 h (900)	orange, glassy	B_2S_2Se
2 B + 1.5 S + 1.5 Se	1 h (900)	inhomogeneous	B_2S_3 + BSe_2 + subselenide
2 B + S + 2 Se	1 h (900)		
2 B + 3 S + Se	1 h (900)	inhomogeneous	B_2S_3 + BS_2 + BSe_2 (major)
2 B + 2 S + 2 Se	1 h (900)	inhomogeneous	B_2S_3 + BS_2 + BSe_2 (minor)
2 B + S + 3 Se	1 h (900)	inhomogeneous	BS_2 + BSe_2
B + x Te ($1 < x < 2$)	1 h (1200) (variable conditions)	inhomogeneous	B + Te
B + Se + Te	1 h (1200)	inhomogeneous	B + Te + BSe_2 + subselenide

behavior can serve as a noninvasive qualitative measure of sample crystallinity.

Within the frame of the present study a bifold research objective is pursued. The power of ^{11}B NMR to function as a diagnostic tool in boron–chalcogenide chemistry is examined, and the spectroscopic parameters are related to the solid-state properties of these materials.

Experimental Section

The syntheses were carried out in evacuated silica ampules, using amorphous boron (97%), DAB-6 sulfur, and LAB selenium (99.5%). Since the signal of elemental boron can be easily distinguished from those of the products, the progress of the reaction can be studied by monitoring the boron resonance. Also, the chemical attack of the silica glass ampules involving reactions such as

$$2B_2S_3 + 3SiO_2 \rightarrow 2B_2O_3 + 3SiS_2$$

can be easily detected by NMR. The spectra show that it is possible to suppress this undesired side reaction by using graphitized ampules.[21]

NMR spectra were taken with a Varian V 4200 B spectrometer with a crossed coil probe arrangement. The operating frequency was set close to 7.00 MHz. The rf power level was varied over a broad range before it was adjusted with respect to the observed relaxation behavior. Spectra were recorded by using the classical modulated field sweep technique and accumulated by a Northern TRACOR multichannel analyzer. After the NMR measurement the samples were opened in an inert atmosphere and characterized by X-ray single-crystal and powder diffraction, chemical analysis, and various physicochemical techniques. Table II specifies the optimum reaction conditions, the observed product morphology, and the product distribution inferred from both NMR and physicochemical investigation.

Results and Discussion

Boron–Sulfur System. Figure 2 shows the variation of the spectra as a function of the S:B ratio. At and below the ratio of 3:2, glassy B_2S_3 is the main reaction product. The observed spectrum of this compound is in good agreement with previous studies of B_2S_3.[22-24] At higher sulfur contents, however, the saturation behavior indicates that the samples are crystalline. While the spectra indicate that the boron coordination is still triangular, the electric quadrupole coupling constant is found to be considerably lower than in B_2S_3. In addition, X-ray studies on single crystals synthesized within these samples indicate the formation of two isomeric compounds of stoichiometry BS_2, the crystal structures of which have been recently solved.[6,25,26] They consist of five-membered B_2S_3 rings connected by sulfur atoms to form polymeric chains or B_8S_{16} molecules, respectively (cf. Figure 3). The observation of distinct and uniform NMR signals with a quadrupole coupling clearly weaker than that of B_2O_3

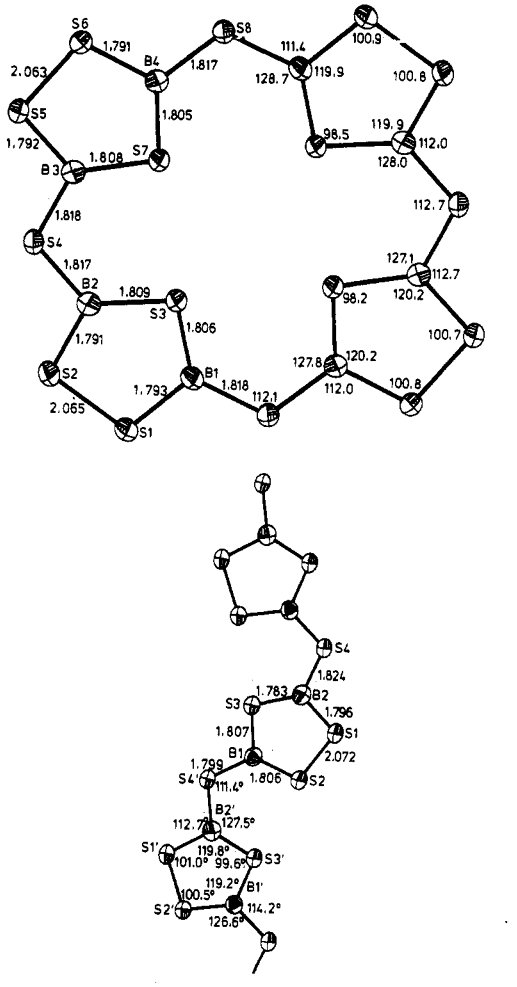

Figure 3. Structures of B_8S_{16} (top) and polymeric BS_2 (bottom) with bond lengths (Å) and bond angles (deg).[6,21,25,26] The coordination of boron is exactly planar in both phases.

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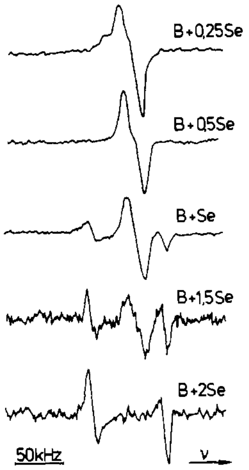

Figure 4. Variation of the ^{11}B NMR spectra in the system B-Se as a function of composition.

reveals that the bulk material consists of these $(BS_2)_n$ chains or rings, and no B_2S_3 is formed under these conditions. Moreover, the compositional dependence of the spectra in Figure 2 shows no evidence of a compound B_2S_5 that has been proposed recently.[9] This result is in agreement with thermochemical data, suggesting the nonexistence of this compound.[13]

Boron-Selenium System. Figure 4 displays the results of an analogous study in the system B-Se. Already at very low Se contents (Se:B = 0.25) significant changes in the spectra indicate the formation of a compound. The line width amounts to ca. 20 kHz, independent of Larmor frequency, hence indicating the absence of second-order quadrupole effects and reflecting strong dipolar coupling. The experimental second moment suggests that boron is involved in at least two B-B bonds. On the other hand, no X-ray information could be obtained because this material is amorphous. The resonance line pertaining to this "subselenide" is observed up to a 2:3 B:Se ratio. In addition, a signal indicating boron in threefold chalcogen coordination is observed in this compositional region. The numerical value of the coupling constant suggests that the compound formed is the selenium analogue to BS_2 rather than to B_2S_3. Additional support comes from the observation that, in contrast to the B-S system, a batch of 2 B + 3 Se yields an inhomogeneous product while at a 1:2 ratio single-site NMR spectra are observed. The above prediction was verified by single-crystal X-ray diffraction, and the structure of BSe_2 is completely analogous to that of the polymeric chainlike BS_2.[6,26,27] When the selenium content is increased beyond a Se:B ratio of 2:1, the lineshape remains unaffected while the relaxation behavior indicates progressive tendency to vitrification in agreement with earlier results.[8]

Synthetic parameters, the melting point, and the X-ray powder pattern of BSe_2 agree with some data in the literature, where they are, however, assigned to a compound of stoichiometry B_2Se_3[12-14] (for details see also[21,27]). The present study, however, casts doubt upon the formation of this compound under the applied high-temperature conditions. Red BSe_2 dominates the system at high selenium content while at low content a yellowish amorphous subselenide is formed. In the following, the stoichiometry of the latter will be addressed.

In the literature subselenide compounds of stoichiometries B_4Se and B_2Se have been published, none of which appears to be well characterized. Thermogravimetric data taken on BSe_2 indicate that this compound, depending on the experimental conditions, can decompose with volatilization of elemental selenium to yield amorphous residues that have the net compositions of either BSe or B_2Se.[27]

In an attempt to elucidate the stoichiometry of the subselenide the quantitative ratio of subselenide:BSe_2 formed in a sample of known batch composition (B:Se = 2:3) was determined. This can be done by NMR because the signals reflecting both compounds are well discriminated in the spectrum. Since the spin-lattice relaxation times of both phases are very different, the radio frequency power level was carefully adjusted in order to prevent erroneous results by undesired saturation effects. Figure 5 showing the integrated signal of this sample indicates that the absolute boron contents of both phases are roughly the same in this sample. Both phases were then separated by sublimation (BSe_2 sublimes from the solid material at 450 °C (10^{-4} bar),[21,27]) and their mass ratio was determined to be 1:1.2. As can be seen from Table III these results are only compatible with a BSe stoichiometry while a B_2Se composition can be ruled out. In view of the amorphous character of the subselenide it cannot be excluded, however, that the stoichiometry in this material may be variable to some extent.

Figure 5. Integrated line shape of a sample made from the batch 2 B + 3 Se.

Table III. Elucidation of the Boron-Subselenide Stoichiometry by Gravimetric Determination and NMR Analysis of the Mixture Formed in the Batch 2 B + 3 Se (Experimental Values in Parentheses)

reaction	mass ratio[a]	abs B content ratio[a]
$6\ B + 9\ Se \rightarrow B_2Se + 4\ BSe_2$	1:6.7 (1:2)	1:2 (1:1.2)
$2\ B + 3\ Se \rightarrow BSe + BSe_2$	1:1.9	1:1

[a] Subselenide:BSe_2.

Boron-Sulfur-Selenium System. From the previous sections it is clear that boron displays characteristically different chemical behavior toward sulfur and selenium. In view of this difference it is interesting to study the products arising from competitive reactions when both chalcogens are present. To this end, samples corresponding to an overall stoichiometry B_2X_3 and BX_2 using varying S:Se ratios were studied. The NMR spectra show that about one-third of S in glassy B_2S_3 can be substituted with selenium without destroying the homogeneity. At higher selenium contents the spectra indicate demixing into B_2S_3, BSe_2, and subselenide, which can be distinguished in a similar way as shown in Figures 2 and 4. Also, no homogeneous "mixed" dichalcogenides are observed.

Boron-Tellurium System. No sp^2-hybridized boron compound was found in batches of varying boron:tellurium ratios to which a wide range of synthetic conditions had been applied.

Moreover the broad line observed in the ^{11}B spectra closely resembles that of amorphous boron and does not permit the identification of eventually formed "subtelluride" as compared to the B-Se system. Furthermore, attempts to replace some selenium by tellurium in the compound BSe_2 were unsuccessful according to the NMR result. The results agree with an earlier study from which the nonexistence of binary boron-tellurium compounds was inferred.[16] The trend observed in the reactivity of boron toward the chalcogens can be understood in terms of sharply decreasing bond energies. Whereas, under ordinary conditions, the system boron-oxygen is completely dominated by B_2O_3, with sulfur B_2S_3 as well as BS_2 (which contains an S-S bond) is formed. With selenium, disproportionation into BSe_2 and subselenide prevails, reflecting already the less effectve competition of boron-chalcogen bonds compared to boron-boron and chalcogen-chalcogen bonds. With tellurium, energetic preconditions are obviously so unfavorable that no bond formation occurs.

Chemical Bond Properties of B_2S_3, BS_2, and BSe_2. Figures 6 and 7 show the experimental spectra of BS_2 and BSe_2, which were fitted in terms of e^2qQ and η with the line-shape simulation

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(27) Hürter, H.-U.; Krebs, B.; Brendel, C., to be submitted for publication.

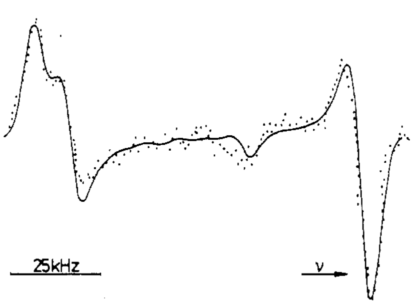

Figure 6. ^{11}B NMR spectrum of BS_2 at 7.02 MHz. The solid line represents the single-site fit listed in Table IV.

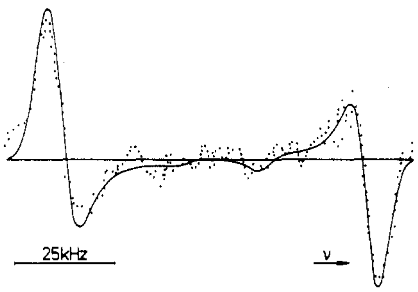

Figure 7. ^{11}B NMR spectrum of BSe_2 at 7.02 MHz. The solid line represents the single-site fit listed in Table IV.

Table IV. Quadrupole Coupling Constants and Asymmetry Parameters in the Subject Compounds Obtained by Computer Simulation

compd	e^2qQ/h, MHz	η	compd	e^2qQ/h, MHz	η
B_2S_3	2.455	0.06	BSe_2	2.070	0.05
BS_2	2.160	0.10			

program of Taylor and Bray.[19] It should be noted here that the fits of Table IV are unique if the discrete site hypothesis[28] is applicable. In the presence of inhomogeneous broadening, however, the spectra observed may also reflect a zero asymmetry parameter and a distribution of e^2qQ.[29] Owing to this uncertainty, the significance of the η values remains, as in many ^{11}B solid-state applications, an open question and shall be omitted in the subsequent discussion. On the other hand, interesting information about bond properties is available from the e^2qQ/h data. Electric quadrupole coupling constants in boron compounds are frequently interpreted in terms of the Townes–Dailey method,[30] which considers the p-electron imbalance at the boron atoms as the main contribution to the electric field gradient. In the case of sp^2 hybridization e^2qQ/h (^{11}B) = 5.39 MHz has been predicted[31] and subsequently almost quantitatively verified in alkylboron compounds.[32] In most triangular substances, bond polarity effects as well as back-donation of nonbonding substituent electrons into the empty boron p_z orbital lead to experimental values about half as large as those theoretically predicted. Since the above effects are difficult to separate, only quadrupole couplings should be compared of compounds that have very similar bond polarities. This condition is certainly fulfilled for the compounds that are the subject of the present investigation. The aforementioned analysis of quadrupole coupling data indicates that the boron–chalcogen bonds in BS_2 and BSe_2 have significantly higher π character than in B_2S_3. This is probably due to the fact that within the five-membered rings the constituents of the S–S and Se–Se bridges supply significantly large amounts of electron density to the boron atom. This kind of behavior has been also revealed by CNDO/2 studies of B_8S_{16}[33] as well as of dihalotrithiadiborolanes[34] and has led to speculations about the possibility of electron delocalization as it is, for instance, observed in borazenes. While, e.g. for 2,4,6-trichloroborazene, the electric quadrupole constant vanishes, thus indicating full π character of the B–N bonds,[35] it is clear from the data in the present study that no appreciable electron delocalization is possible in the BS_2 and BSe_2 trichalcogenadiborolane rings. This result agrees well with conclusions drawn from ^{11}B NMR chemical shift data on the dihalotrithiadiborolanes,[36] which contain the same five-membered rings. Nevertheless, the present study indicates that ^{11}B solid-state NMR can serve as a sensitive measure of bonding characteristics in boron chalcogenide systems. This makes it a valuable tool in order to design appropriate compounds in which the electronic features can be correlated with structural properties.

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Registry No. BS_2, 12045-25-9; BSe_2, 12505-78-1; B, 7440-42-8; S, 7704-34-9; Se, 7782-49-2; Te, 13494-80-9; ^{11}B, 14798-13-1.

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Assignment of the Deuteron NMR Spectra of Chromium(III) Complexes with edta and Related Ligands

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The deuteron NMR spectra of [Cr(cdta)]$^-$, [Cr(pdta)]$^-$, [Cr(edta)]$^-$, and [Cr(edda)(mal)]$^-$ have been assigned by using stereospecific isotopic substitution of cdta and pdta coordinated to substitution-inert Cr(III) and Co(III). Deuteron NMR spectroscopy demonstrates that the Cr(III) complexes of cdta and pdta are structurally similar to [Cr(edta)]$^-$ whose structure was determined to be sexidentate at intermediate pHs in a previous study. The present study also provides the first example of stereospecific isotopic substitution to be carried out on Cr(III).

Introduction

Until recently it was not thought possible to do NMR studies on the paramagnetic complexes of substitution-inert chromium(III). We have demonstrated that deuteron NMR spectroscopy can be used to characterize the solution structures of simple Cr(III) complexes,[2,3] and more recently this method has been extended

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