Inorganica Chimica Acta, 172 (1990) 35–39

Synthesis and Characterization of Pseudohaloborane Adducts of some Heteroaromatic N-bases

MRINAL K. DAS* and PRADIP K. MAITI

Department of Chemistry, Jadavpur University, Calcutta 700032 (India)

(Received September 18, 1989)

Abstract

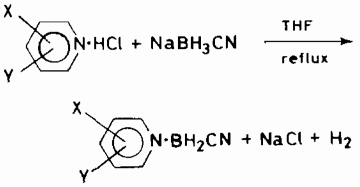
Six cyanoborane adducts of the heteroaromatic amines, 2-amino-, 3-amino-, 4-amino-, 2-amino-4-methyl-, 4-cyano- and 4-ethylpyridines, and four isothiocyanatoborane adducts of the heteroaromatic amines, 3-methyl-, 4-methyl-, 4-ethyl- and 4-amino-pyridines have been prepared. These have been characterized by elemental analyses and by infrared and ^{1}H and ^{11}B NMR spectral study.

Introduction

Cyanoborane adducts of aliphatic amines have attracted considerable attention in terms of synthesis [1–8], hydrolytic studies [2, 9] and biological activity studies [10] as they are the precursors to the amine–carboxyboranes [11], the boron analogues of amino acids. However, relatively very little information is available about the pseudohaloborane adducts of heterocyclic aromatic N-bases [5, 6, 12a]. Recently we described a general method for the synthesis of isothiocyanatoborane adducts of alkylamines [13]. We now report here the syntheses and characterization of a few cyanoborane adducts of heteroaromatic N-bases and the applicability of the general synthetic procedure developed earlier for the synthesis of isothiocyanatoborane adducts of heteroaromatic N-bases.

Results and Discussion

Various methods for the synthesis of amine–cyanoboranes have been reported in the literature [1–7]. These involve primarily the reaction of $NaBH_3CN$ with an amine in the presence of HCl in ethereal solvents [1, 2, 12], the reactions of the *in situ* generated $(BH_2CN)_n$ from $NaBH_3CN$ [6] with an amine [6, 12], or amine exchange from methylamine–cyanoborane [7]. However, the most useful general method is the reaction of amine hydrochloride with $NaBH_3CN$ for those amines which easily form hydrochlorides [5, 8]. Pyridine–cyanoborane and picoline–cyanoboranes have been prepared, respectively, by the reaction of the hydrochlorides with $NaBH_3CN$ [5] and by the reaction of the bases with $(BH_2CN)_n$ [6]. The amine–cyanoboranes reported here have been prepared by the general method involving the reaction of the heterocyclic N-base hydrochlorides with $NaBH_3CN$ in refluxing THF (eqn. (1)).



(1)

$(X = 2\text{-}NH_2,\ 3\text{-}NH_2,\ 4\text{-}NH_2,\ 4\text{-}CN,\ 4\text{-}C_2H_5,\ Y = H;\ X = 2\text{-}NH_2,\ Y = 4\text{-}CH_3)$

The cyanoborane adducts (**1**–**6**) as described by eqn. (1) were obtained in good yields (66–86%). Excepting **2** and **6** which are colourless liquids, all compounds are colourless air stable solids at room temperature. The analytical data, melting points (m.p.), yields and characteristic infrared and NMR spectral data are given in Table 1.

In the infrared spectra of the four aminopyridine–cyanoboranes (**1**–**4**), absorptions in the range 3471–3344 cm^{-1} are assigned to the stretchings modes of the NH_2 group in consonance with the aminopyridine–boranes described earlier [14]. The $\nu(NH_2)$ modes in the latter compounds have been shown to occur in the range 3460–3180 cm^{-1}. For the aminopyridines there are three possibilities of binding with BH_2CN as with BH_3. First, a BH_2CN group may bind to a ring nitrogen; second, it may bind to the nitrogen in the NH_2 group; and third, two BH_2CN groups may be bound to the nitrogens of both the pyridine ring and the NH_2 group. However, analytical data indicate the presence of one BH_2CN group, thus limiting the

---

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

TABLE 1. Physical, analytical and spectral data of heteroaromatic N-base–cyanoboranes and isothiocyanatoboranes

Compound	Formula	Yield (%)	Melting point (°C)	Analysis: found (calc.) (%)				IR data (cm^{-1})[a]			NMR data (δ in ppm)[b]			
				C	H	N	B	ν(NH)	ν(BH)	ν(CN)	^{1}H NMR			^{11}B NMR
											Aryl	CH_3	CH_2	
1	$2\text{-}NH_2C_5H_4N\cdot BH_2CN$	86	104	53.80 (54.20)	6.01 (6.06)	31.43 (31.60)	8.17 (8.13)	3438s 3344s	2425s 2398s	2192s	6.7–8.2(m)			−20.7(t)
2	$3\text{-}NH_2C_5H_4N\cdot BH_2CN$	66	liquid	52.07 (54.20)	6.34 (6.06)	31.83 (31.60)	8.69 (8.13)	3466s 3367s	2413s	2175s	7.1–8.1(m)			−15.9(br)
3	$4\text{-}NH_2C_5H_4N\cdot BH_2CN$	72	126	54.27 (54.20)	6.02 (6.06)	31.49 (31.60)	8.02 (8.13)	3416s 3347s	2416s 2393s	2190s	6.6–8.0(m)			−17.5(t)
4	$2\text{-}NH_2,4\text{-}CH_3C_5H_3N\cdot BH_2CN$	81	110	56.78 (57.20)	6.63 (6.86)	27.59 (28.59)	7.53 (7.35)	3471s 3361s	2422s 2347s	2190s	6.6–7.9(m)	2.25(a)		−19.7(t)
5	$4\text{-}CNC_5H_4N\cdot BH_2CN$	82	134	57.77 (58.82)	4.14 (4.23)	28.91 (29.39)	7.8 (7.56)		2429s	2245s 2196s	7.8–8.9(m)			−15.4(t)
6	$4\text{-}C_2H_5C_5H_3N\cdot BH_2CN$	79	liquid	64.65 (65.81)	7.23 (7.59)	18.65 (19.91)	7.85 (7.40)		2420s 2320s	2177s	7.5–8.5(m)	1.38(t)	2.54(q)	−16.1(t)
7	$3\text{-}CH_3C_5H_4N\cdot BH_2NCS$ [d]	77	liquid	49.96 (51.22)	5.24 (5.48)	16.87 (17.07)	6.98 (6.61)		2420s	2120s	7.6–8.8(m)	2.6(s)		[c]
8	$4\text{-}CH_3C_5H_4N\cdot BH_2NCS$	85	96	50.8 (51.22)	5.46 (5.48)	17.13 (17.03)	7.01 (6.61)		2430s	2150s	7.5–8.5(m)	2.6(s)		−7.1(t)
9	$4\text{-}C_2H_5C_5H_4N\cdot BH_2NCS$	57	72	52.81 (53.93)	5.73 (6.18)	14.51 (15.73)	6.48 (6.22)		2440s	2160s	7.44–8.46(m)	1.4(t)	2.9(q)	−8.2(t)
10	$4\text{-}NH_2C_5H_4N\cdot BH_2NCS$ [d]	52	78	41.56 (43.63)	3.94 (4.84)	24.35 (25.45)	6.81 (6.56)	3380s 3220s	2440s	2160s	6.6–8.2(m)			−7.5(t)

[a] s = strong, m = medium.

[b] s = singlet, t = triplet, q = quartet, m = multiplet.

[c] Does not have enough shelf-life to obtain ^{11}B NMR spectra.

[d] Very hygroscopic in nature.

possibilities to the first two. Previously, from an infrared spectral study, it was concluded that the BH_3 group was attached to the pyridyl nitrogen and not to the NH_2 nitrogen. Had it been attached to the NH_2 group, there should be considerable shift in stretching modes of the NH_2 group in the adducts to lower energy compared to those in the free amines. But no such change was observed thereby substantiating the assumption [14]. In the present study the $\nu(NH_2)$ modes in the compounds **1–4** occur in the range of 3471–3344 cm^{-1}, which compares very favourably to those of the corresponding borane adducts. Moreover, the experimental evidence in favour of bonding through pyridine nitrogen comes from the results of two competing reactions, one involving the exchange of pyridine with aniline cyanoborane and the other involving the reaction of hydrochlorides of pyridine and aniline with $NaBH_3CN$; both reactions yielded pyridine–cyanoborane as the product, substantiated by m.p. (34 °C, lit. 34–35 °C [5]) and infrared spectra. In the rest, there are no free NH_2 groups and their absence is borne out by the infrared spectra.

The $\nu(CN)$ modes in the cyanoborane adducts **1–6** appear as strong absorptions at 2245–2175 cm^{-1}. The $\nu(CN)$ bands reported for aliphatic amine–cyanoboranes [4–8] are in the range 2280–2170 cm^{-1}, whereas those for the cyanoborane adducts of pyridine and α-, β- and γ-picolines [6] were reported to be at 2250–2190 cm^{-1} and for quinuclidine–cyanoborane at 2220 and 2180 cm^{-1} [7]. The infrared spectra of both trimethylamine–cyanoborane and trimethylamine–isocyanoborane were investigated by Vidal and Ryschkewitsch [15]. It was found that the $\nu(CN)$ mode of the cyanoborane adduct appeared at 2230 cm^{-1} whereas that for isocyanoborane adduct appeared at 2135 cm^{-1}, 95 cm^{-1} lower than that for the cyano isomer. Also from an X-ray crystal structure study of $NH_3{\cdot}BH_2(CN)$ [16] it was shown that the cyano group was bonded to boron through the carbon end. In the compounds **1–6** reported here the $\nu(CN)$ modes appear in the range 2245–2175 cm^{-1}, and therefore it may be concluded that the mode of binding in the said compounds is through carbon rather than through nitrogen of the CN group. For 4-cyanopyridine–cyanoborane there are two well separated bands at 2245 and 2196 cm^{-1} indicating the presence of two different types of cyano groups. From a comparison of the $\nu(CN)$ in other heteroaromatic N-base–cyanoboranes and 4-cyanopyridine–cyanoborane (**5**) with that of 4-cyanopyridine itself, it may be concluded that in the latter compound the band at 2196 cm^{-1} is due to the CN group attached to boron while the band at 2245 cm^{-1} results from $\nu(CN)$ of the pyridine ring [$\nu(CN)$ in 4-cyanopyridine is at 2243 cm^{-1}]. The $\nu(B–H)$ modes of the compounds **1–6** have been observed as strong bands in the range 2429–2320 cm^{-1} and those in α-, β- and γ-picoline–cyanoboranes in the range 2420–2370 cm^{-1} [6] while those in 2-amino-, 3-amino- and 4-amino-pyridine–boranes absorb in the range 2370–2260 cm^{-1} [14]. Thus the $\nu(B–H)$ modes found for the compounds reported here are in conformity with those found earlier [6, 14].

In the NMR spectra of the heteroaromatic N-base–cyanoboranes (**1–6**), the presence of aromatic protons was observed in their usual positions. Also, in 2-amino-4-methylpyridine–cyanoborane (**4**) and 4-ethylpyridine–cyanoborane (**6**), the presence of methyl and ethyl groups has been observed. The signals for NH_2 and BH_2 protons, however, could not be detected. In the ^{11}B NMR spectra of the compounds **1–6**, the ^{11}B NMR signals appear between δ −15.4 and −20.7. The ^{11}B NMR data of the amine–cyanoboranes are so far limited. The $\delta(^{11}B)$ for quinuclidine–cyanoborane [7] was found at −15.2 with $^1J(^{11}B–^1H)$ of 103 Hz. For trimethylamine–cyanoborane $\delta(^{11}B)$ values of −15.2 [1] and −14.9 [17] have been reported. Further reported $\delta(^{11}B)$ values are −15.3 for *N*-methylmorpholine–cyanoborane and −20.5 for morpholine–cyanoborane with $^1J(^{11}B–^1H)$ of 98.5 Hz [17]. The data obtained for the compounds reported here are in consonance with those noted above and that the boron nucleus in these compounds is highly shielded and the boron atoms are four-coordinate in nature.

Isothiocyanatoborane adducts reported here are prepared by the reaction of heteroaromatic N-base hydrochlorides with $NaBH_3SCN$, generated *in situ* from $NaBH_4$, iodine and NaSCN in monoglyme according to the following scheme [13]

$$NaBH_4 + \tfrac{1}{2}I_2 \xrightarrow[\text{r.t.}]{\text{monoglyme}} BH_3{\cdot}\text{monoglyme} + NaI + \tfrac{1}{2}H_2$$

$$BH_3{\cdot}\text{monoglyme} + NaSCN \longrightarrow NaBH_3SCN\ (\text{in monoglyme})$$

$$NaBH_3SCN\ (\text{in monoglyme}) + X\text{-}C_5H_4N{\cdot}HCl \xrightarrow{\text{reflux}} X\text{-}C_5H_4N{\cdot}BH_2NCS + NaCl + H_2$$

The isothiocyanatoboranes of trimethylamine [19] and ammonia [18, 20] have been known for some time. However, the only isothiocyanatoborane adduct of a heteroaromatic N-base known so far is pyridine–isothiocyanatoborane [21] prepared by the exchange of iodine by the thiocyanate group from $C_5H_5N{\cdot}BH_2I$ by the action of silver thiocyanate involving a two-step process [21]. 3-Methylpyridine–isothiocyanatoborane (7) and 4-methylpyridine–

isothiocyanatoborane (**8**) were obtained in 85% and 77% yields, respectively, whereas the yields of 4-ethylpyridine–isothiocyanatoborane (**9**) and 4-aminopyridine–isothiocyanatoborane (**10**) were comparatively low being 57% and 52%, respectively. All the compounds are colourless solids except 3-methylpyridine–isothiocyanatoborane which is a colourless liquid. Adducts derived from 3-methylpyridine and 4-aminopyridine (**7** and **10** respectively) are highly air and moisture sensitive materials. The liquid (**7**) obtained was of satisfactory purity as evident from spectra and analytical data, but further purification was not attempted considering its sensitivity to air and moisture. Their physical and spectral data are given in Table 1.

In the infrared spectra, the $\nu(NH_2)$ modes for 4-aminopyridine–isothiocyanatoborane (**10**) occur at 3380 and 3220 cm^{-1} for the free NH_2 group. The $\nu(B-H)$ modes of the compounds **7**–**10** are found in the region 2440–2420 cm^{-1}. The $\nu(B-H)$ modes in $C_5H_5N\cdot BH_2NCS$ [21] and $Me_3N\cdot BH_2NCS$ [19] were reported to occur at 2430 and 2433 cm^{-1}, respectively. The bands in the region 2180–2120 cm^{-1} were assigned to the $\nu(CN)$ modes in analogy with those for the isothiocyanatoborane adducts of aliphatic amines ($\nu(CN)$, 2140 cm^{-1}) [13] and $Me_3N\cdot BH_2NCS$ ($\nu(CN)$, 2140 cm^{-1}) [19] and pyridine–isothiocyanatoborane ($\nu(CN)$, 2130 cm^{-1}) [21]. An X-ray crystal structure study of $H_3N\cdot BH_2NCS$ [20] indicates that boron is nitrogen bonded and not sulphur bonded. These observations suggest that the compounds obtained are rather isothiocyanatoborane adducts of the heteroaromatic N-bases, similar to those of the aliphatic amines.

In the NMR spectra of the compounds **7** and **8** the methyl protons on the aromatic ring absorb at δ 2.6 ppm as singlets, and in **9** the methyl protons absorb at δ 1.4 and the CH_2 protons absorb at δ 2.9 in the usual ethyl pattern. The aromatic protons show multiplets in the region δ 6.6–8.8 in all the compounds. In the ^{11}B spectra of the compounds, the $\delta(^{11}B)$ occur at −7.1 to −8.2. This is indicative of the tetracoordinate nature of boron attached to electronegative groups.

Experimental

All chemicals used were of reagent grade quality unless otherwise mentioned. 2-Amino-, 3-amino-, 4-amino-, 2-amino-4-methyl- and 4-cyanopyridines were reagent grade commercial products and were used as received. 3-Methyl-, 4-methyl- and 4-ethylpyridines were dried by refluxing over solid KOH and were distilled prior to use. All the bases were converted to their hydrochlorides by bubbling dry HCl gas through their ethereal solutions and were finally dried in vacuum. Ether was dried over anhydrous $CaCl_2$ followed by refluxing over sodium. Monoglyme and benzene were dried by refluxing over sodium. Tetrahydrofuran (THF) was dried by refluxing over sodium and then over $LiAlH_4$. All the solvents were distilled prior to use. $NaBH_3CN$ (Aldrich, U.S.A.) and $NaBH_4$ (Loba, India) were used as received.

Infrared spectra were recorded on a Perkin-Elmer model 597 or 883 spectrophotometer. Proton NMR spectra were recorded on a Jeol JNM FX-100 or Varian EM 390 and the δ values are with reference to TMS as internal standard. The ^{11}B NMR spectra were recorded on a Varian XL 200, a Bruker WH 360 or a Bruker AP 200 MHz spectrometer. The δ values (in ppm) are with reference to $BF_3\cdot O(C_2H_5)_2$ as external standard. A controlled atmosphere glove box (Labconco Corpn., Kansas City, MO, U.S.A.) was used for inert atmosphere handlings.

Elemental (C, H, N) analyses of solid samples were done on a Perkin-Elmer 240C elemental analyser. The liquid samples were analysed at the microanalytical laboratory of Calcutta University. Boron was estimated volumetrically in the presence of mannitol [22] after decomposition of the samples in presence of triple catalyst ($CuSO_4:K_2SO_4:Se = 6:2:1$) [23].

Synthetic Procedures

(i) Cyanoborane adducts of heteroaromatic N-bases

$NaBH_3CN$ (1.89 g, 30 mmol) and an appropriate N-base hydrochloride (30 mmol) were placed in a three necked flask fitted with a reflux condenser, a magnetic stirrer and a gas bubbler, and the assembly was flushed with dry nitrogen. THF (40 ml) was then added through a side arm and the mixture was refluxed for *c.* 48 h. When the evolution of hydrogen gas ceased, the mixture was cooled and filtered in a sintered glass funnel to remove solid residue. The crude amine–cyanoboranes were obtained by removing the solvent in a rotary evaporator. All the N-base–cyanoboranes (except **2** and **6**) are solids and were purified by recrystallization from hot water. 3-Aminopyridine–cyanoborane (**2**) and 4-ethylpyridine–cyanoborane (**6**) were liquids. These two compounds were purified by mixing the compounds with *c.* 10 ml of distilled water and then extracting them with ether several times followed by drying the ether extract over anhydrous $MgSO_4$ and evaporating under reduced pressure. Their data are given in Table 1.

(ii) Competing reactions

(a) Exchange reaction of aniline cyanoborane with pyridine. Aniline cyanoborane (3.96 g, 30 mmol), pyridine (1.10 g, 30 mmol) and THF (30 ml) were refluxed for 48 h in a three necked flask assembled as in (i). Then the solvent was evaporated in a rotary

evaporator and finally in high vacuum at 50 °C when a thick liquid was obtained. On cooling to room temperature, pyridine cyanoborane separated out as colourless solid. Yield 60%.

(b) Reaction of $NaBH_3CN$ with a mixture of aniline hydrochloride and pyridine hydrochloride. In a three necked flask assembled as in (i), a mixture of aniline hydrochloride (3.60 g, 30 mmol), pyridine hydrochloride (3.50 g, 30 mmol) and $NaBH_3CN$ (1.89 g, 30 mmol) were refluxed in THF (40 ml) for 48 h. This was then filtered to remove NaCl. The product pyridine cyanoborane was obtained from the filtrate by a work up similar to that in (a). Yield 55%.

(iii) Preparation of isothiocyanatoborane adducts of heteroaromatic N-bases

$NaBH_4$ (1.14 g, 30 mmol) and NaSCN (2.43 g, 30 mmol) were placed in a three necked flask assembled as in (i) and the system was flushed with dry nitrogen. Monoglyme (35 ml) was then added to it. A solution of iodine (3.81 g, 30 mmol) in monoglyme (15 ml) was added dropwise at room temperature followed by refluxing for 1 h. The mixture was then filtered and the filtrate added to an appropriate amount of N-base hydrochloride in monoglyme (35 ml) taken in another flask assembled as before. This was stirred at room temperature for 18 h under nitrogen atmosphere. The solvent was removed after filtration in vacuum to obtain the crude products. The solid crude products (8–**10**) were purified by recrystallization from chloroform and petroleum ether (40–60°) mixture. Compound 7 was obtained as a liquid and purified by extracting the crude product with dry benzene and evaporating the solvent and drying in vacuum. Their characterization data are given in Table 1.

Acknowledgements

The authors sincerely thank the Department of Science and Technology, New Delhi, for a research grant (to M.K.D.) and the Council of Scientific and Industrial Research for a fellowship (to P.K.M.). The authors are indebted to Professor H. Nöth of the University of Munich (F.R.G.), Professor K. Niedenzu of the University of Kentucky (U.S.A.), and Professor G. Srivastava of Rajasthan University (India) for the ^{11}B NMR spectra. Our special thanks are due to Professor H. Nöth for offering many valuable suggestions and advice.

References

1 S. S. Uppal and H. C. Kelly, *Chem. Commun.*, (1970) 1619.
2 C. Weidig, S. S. Uppal and H. C. Kelly, *Inorg. Chem.*, *13* (1974) 1763.
3 G. E. Ryschkewitsch and V. R. Miller, *J. Am. Chem. Soc.*, *95* (1973) 2836.
4 O. T. Beachley, Jr. and B. Washburn, *Inorg. Chem.*, *14* (1975) 120.
5 P. Wisian-Neilson, M. K. Das and B. F. Spielvogel, *Inorg. Chem.*, *17* (1978) 2327.
6 D. R. Martin, M. A. Chiusano, M. L. Denniston, D. J. Dye, E. D. Martin and B. T. Pennigton, *J. Inorg. Nucl. Chem.*, *40* (1978) 9.
7 B. Kemp, S. Kalbag and R. A. Geanangel, *Inorg. Chem.*, *23* (1984) 3063.
8 M. K. Das, P. Maiti and P. Mukherjee, *Indian J. Chem.*, *24A* (1985) 47.
9 (a) B. F. Spielvogel, F. Harchelroad, Jr. and P. Wisian-Neilson, *J. Inorg. Nucl. Chem.*, *41* (1979) 1223; (b) K. D. Hargrave, A. T. McPhail, B. F. Spielvogel and P. Wisian-Neilson, *J. Chem. Soc., Dalton Trans.*, (1977) 2150.
10 (a) I. H. Hall, C. O. Starnes, A. T. McPhail, P. Wisian-Neilson, M. K. Das, F. Harchelroad, Jr. and B. F. Spielvogel, *J. Pharm. Sci.*, *69* (1980) 1025; (b) I. H. Hall, M. K. Das, F. Harchelroad, Jr., P. Wisian-Neilson, A. T. McPhail and B. F. Spielvogel, *J. Pharm. Sci.*, *70* (1981) 339; (c) P. Sur, D. K. Roy and M. K. Das, *I.R.C.S. Med. Sci.*, *9* (1981) 1066; (d) I. H. Hall, C. J. Gilbert, A. T. McPhail, K. W. Morse, K. Hasset and B. F. Spielvogel, *J. Pharm. Sci.*, *74* (1985) 755.
11 (a) M. K. Das and P. Mukherjee, *J. Chem. Res. S*, (1987) 368; *J. Chem. Res. M*, (1987) 2981; (b) M. K. Das and P. Mukherjee, *J. Chem. Res. S*, (1985) 66; (c) B. F. Spielvogel, L. Wojnowich, M. K. Das, A. T. McPhail and K. D. Hargrave, *J. Am. Chem. Soc.*, *98* (1976) 5702; (d) B. F. Spielvogel, M. K. Das, A. T. McPhail and K. D. Onan, *J. Am. Chem. Soc.*, *102* (1980) 6343.
12 (a) B. Gyori, J. Emri and I. Fehr, *J. Organomet. Chem.*, *222* (1983) 17; (b) B. F. Spielvogel, R. F. Bratton and C. G. Moreland, *J. Am. Chem. Soc.*, *94* (1972) 8597.
13 M. K. Das and P. K. Maiti, *Synth. React. Inorg. Met.-Org. Chem.*, *17* (1987) 617.
14 C. J. Foret, M. A. Chiusano, J. D. O'Brien and D. R. Martin, *J. Inorg. Nucl. Chem.*, *42* (1980) 165.
15 J. L. Vidal and G. E. Ryschkewitsch, *Inorg. Chem.*, *16* (1977) 1898.
16 A. T. McPhail, K. D. Onan, B. F. Spielvogel and P. Wisian-Neilson, *J. Chem. Res. S*, (1978) 205; *J. Chem. Res. M*, (1978) 2601.
17 H. Nöth and B. Wrackmeyer, *Basic Principles and Progress – Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, P. Dielh, E. Fluch and R. Kosfeld (eds.), Springer, Berlin, 1978.
18 V. D. Aftandilian, H. C. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, *83* (1961) 2471.
19 P. J. Bratt, M. P. Brown and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, (1974) 2161.
20 D. S. Kendal and W. N. Lipscomb, *Inorg. Chem.*, *12* (1973) 2920.
21 M. L. Denniston, M. A. Chiusano and D. R. Martin, *J. Inorg. Nucl. Chem.*, *38* (1976) 979.
22 L. H. Thomas, *J. Chem. Soc.*, (1946) 820.
23 R. C. Rittner and R. Culmo, *Anal. Chem.*, *35* (1963) 1268.