665. *Cationic Organoboron Complexes. Part II.*[1]

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Chlorodiphenylborane and 10-chloro-9-oxa-10-bora-anthracene undergo metathesis with silver salts of strong acids in basic solvents to form electrolytic solutions. The structures of these solutions are discussed and their products of reaction with 2,2′-bipyridyl are described. The complexes of 2,2′-bipyridyl with the diphenylboronium ion and with 9-oxa-10-boronia-anthracene are shown to contain a saturated tetrahedral boron atom. Similarly, the 1 : 1 and 2 : 1 complexes of chlorodiphenylborane with 2,2′-bipyridyl are shown to be ionic compounds of the 2,2′-bipyridyldiphenylboronium ion.

AN earlier paper[1] described the preparation of solutions containing the diphenylboronium ion, the structure of which was discussed in terms of a trigonal planar configuration involving the co-ordination of one basic molecule (I). The present paper comprises a further study of the nature of solutions of the diphenylboronium ion together with a more general discussion of the conditions under which co-ordination compounds of boron ionise to form boron-containing cations. There are three possible configurations for the boron atom in such a cation and, in each case, part of the stabilisation must arise through co-ordination of a basic ligand or through conjugation with an aromatic ligand.

(i) sp-*Hybridised boron.* The lowest-energy configuration for a two-co-ordinate cation will be the linear one with *sp*-hybridisation, utilising maximum *s*-orbital and minimum *p*-orbital character. The unfilled *p*-orbitals allow stabilisation through conjugation, while release of steric strain and electronic repulsion forces favour a linear arrangement.

(ii) sp^2-*Hybridised boron.* In trigonal planar configuration, two of the sp^2-hybrids will take part in covalent bond formation, and the third must be filled by an electron pair by co-ordination. The empty *p*-orbital will be available for conjugation with any of the three ligands. In Part I[1] evidence was given that the ion (I) is of this class.

(iii) sp^3-*Hybridised boron.* Tetrahedral cations of boron require the completion of the covalency maximum for first-row elements of the Periodic Table, and the four ligands

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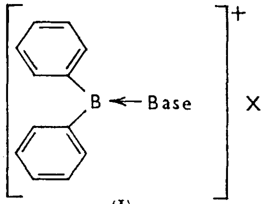
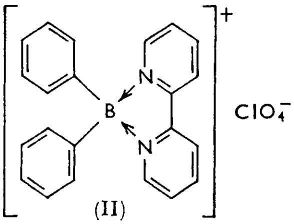
[1] Part I, Davidson and French, *J.*, 1958, 114.

must form two covalent bonds and two dative covalent bonds. Several ions of class (iii) are known [2,3] and 2,2′-bipyridyldiphenylboronium perchlorate (II) is typical.

Chlorodiphenylborane undergoes metathesis with silver salts of strong acids in basic solvents such as dioxan, ethyl methyl ketone, nitrobenzene, or nitromethane. Quantitative yields of silver chloride were obtained by using anhydrous silver hexafluorophosphate, tetrafluoroborate, perchlorate, or perfluorobutyrate. The solutions were yellow and except for those in dioxan were good electrolytes. The 9-oxa-10-bora-anthracene ring system (III) was synthesised [4] in an attempt to prepare a model compound of class (iii), and the metathetic reactions of the chloro-compound (III; R = Cl) appear to be similar to those of chlorodiphenylborane. Nitromethane solution containing equivalent amounts of this substance (III; R = Cl) and of silver perchlorate were mixed, filtered from silver chloride, and treated with one equivalent of trimethylamine. Subsequent addition of ether did not precipitate trimethylamine–9-oxa-10-boronia-anthracene perchlorate (IV; Base = NMe_3). In the salt (IV; Base = NMe_3) the boron atom is part of a pseudo-aromatic nucleus and should be stabilised by increased conjugation with the π-electrons of the benzene rings—an alternative view of the structure would be that a tertiary amine has been quaternised by the heterocyclic group.



(I)



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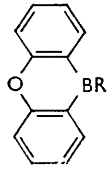
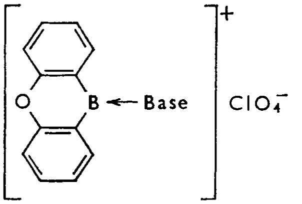
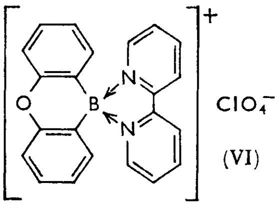


(III)



(IV)



(VI)

Pyridine might be expected to stabilise all types of cation, for not only is it very strongly basic towards acidic boron compounds for steric reasons [5] but also it has π-electron molecular orbitals suitable for stabilisation of a conjugated system. Greenwood and Wade [6] sought evidence for the bimolecular ionisation of the trichloroborane derivative (V) and concluded that the molten complex was not dissociated. A series of complexes derived from 2,2′-bipyridyl has now been prepared, and these prove to be related to the hypothetical dipyridine complex (Va), thus furnishing useful information on the stability of ions of class (iii).

The preparation of the salt (II) has been described previously.[3] Compound (III; R = Cl) undergoes metathesis with silver perchlorate in nitromethane solution, and addition of 2,2′-bipyridyl affords *BB*-2,2′-bipyridyl-9-oxa-10-boronia-anthracene perchlorate (VI). Stoicheiometric addition of the components leads to the expected 1 : 1 and 1 : 2 adducts of 2,2′-bipyridyl with chlorodiphenylborane for which the simple covalent

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[2] Dilthey and Schumacher, *Annalen*, 1906, **344**, 300, 326; Goubeau and Schneider, *Ber.*, 1961, **94**, 816; Parry *et al.*, *J. Amer. Chem. Soc.*, 1958, **80**, 4, 8, 12, 15, 20, 25, 27.

[3] Davidson and French, *Chem. and Ind.*, 1959, 750.

[4] Davidson and French, *J.*, 1960, 191.

[5] Stone, *Chem. Rev.*, 1958, **58**, 101.

[6] Greenwood and Wade, *J.*, 1960, 1130.

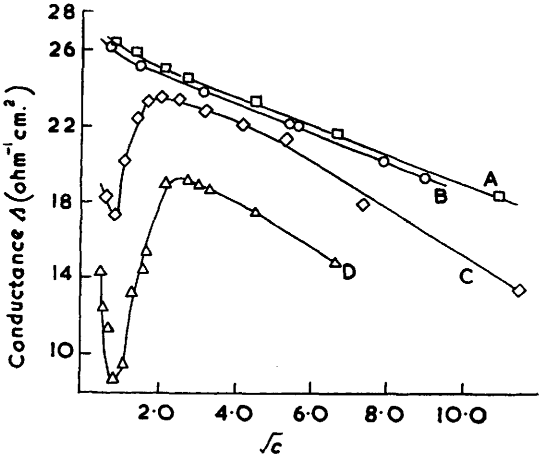
formulæ are (VII) and (VIII). The Figure represents the conductance data for compounds (II), (VI), (VII), and (VIII) which were determined in nitrobenzene solution at 15° in the concentration range 10^{-5}—10^{-2} molar: equivalent conductance is plotted as a function of the square root of concentration.

$$2BCl_3(\text{pyridine})\ (V) \rightleftharpoons [BCl_2(\text{pyridine})_2]^+[BCl_4]^-\ (Va)$$

$$Ph_2BCl(\text{bipy})\ (VII) \rightleftharpoons [Ph_2B(\text{bipy})^+Cl]^-\ (VIIa)$$

$$(Ph_2BCl)_2(\text{bipy})\ (VIII) \rightleftharpoons [Ph_2B(\text{bipy})]^+[Ph_2BCl_2]^-\ (VIIIa)$$

All the physical properties of these compounds are consistent with ionic structures of type (iii), with 2,2′-bipyridyl as a chelating diamine. The ultraviolet absorption in the region of 337 mμ which was characteristic of the conjugated diphenylboronium ion is absent in the case of salt (II) which must therefore contain a saturated boron atom. All four compounds behave as ideal strong electrolytes within certain concentration limits. The linear plots of Λ against $\sqrt{c}$ for salts (II) and (VI) could not be recorded in regions of sufficiently high dilution for accurate extrapolation of Λ_0 which, however, must be very close to 28·0 ohm^{-1} cm.^{2} in both cases. Within experimental error, the two plots are coincident, and hence the Λ_0^+ values for the 2,2′-bipyridyldiphenylboronium and the *BB*-2,2′-bipyridyl-9-oxa-10-boronia-anthracene ions differ by not more than about 1%, as expected for ions of very similar structure and size. Similarly, 2,2′-bipyridylchlorodiphenylborane (VII) and 2,2′-bipyridylbis(chlorodiphenylborane) (VIII) exhibit properties to be expected of chelate derivatives. The former behaves as 2,2′-bipyridyl-diphenylboronium chloride (VIIa) and is a strong electrolyte which has the same infrared spectrum in the solid state as a Nujol mull and in solution in nitromethane (the unusual conductance minimum is discussed below). When perchlorate frequencies are neglected, this spectrum may be superimposed upon the spectrum of (II). The 1 : 2 co-ordination compound fits well into this interpretation as a third salt of the same cation, 2,2′-bipyridyldiphenylboronium dichlorodiphenylborate (VIIIa). It is apparent from the conductance data that the degree of dissociation in solution as measured by Λ/Λ_0 increases through the series of three salts in order of the strengths of the parent acids: $HClO_4 > HBPh_2Cl_2 > HCl$. Whereas these chelate co-ordination compounds are strong electrolytes the parent boronium salts are weak ones and for solutions about 10^{-2}N in nitrobenzene the equivalent conductance of salt (II) is greater than that of diphenylboronium perchlorate[1] by about a factor of ten.



Equivalent conductance in nitrobenzene at 15° of compounds VI (A), II (B), VIII (C), and VII (D).

That the conductances of ions of class (iii) should contrast so sharply with those of other boronium ions is not surprising, as the former contain a saturated boron atom. The formation of a covalent ion-pair requires the fission of one boron–nitrogen bond in the chelate complexes of 2,2′-bipyridyl whereas the formation of an ion-pair from an ion of class (i) or (ii) involves only an electronic rearrangement of π-orbitals. Fission of the boron–nitrogen bond will be manifest in a high activation energy and a low polarisability of the ion. In salt (II) both anion and cation will be resistant to polarisation, and the complex behaves as an ideal strong electrolyte. The similarity of salts (II) and (VI) demonstrates that ions of class (iii) derived from a chelating diamine are thermodynamically more stable than a conjugated ion. Thus (VI) utilises the boron–nitrogen bond rather than the extra conjugation energy of (IV; Base = bipy) for, as described above, complexes of monodentate ligands were not sufficiently stable to be isolated from solution.

It is possible that these differences in degree of dissociation of boronium salts may explain the curious phenomenon of the conductance minimum observed for compounds (VII) and (VIII). This cannot be attributed to ion-pair formation for in a solvent of high dielectric constant such as nitrobenzene the Walden rule ($\varepsilon^3/c_{\text{min.}} = 3 \times 10^4$ moles l.$^{-1}$) predicts that the minima should occur at a much higher concentration.[7] Solutions of materials (VII) and (VIII) more concentrated than about 5×10^{-4}N were quite stable, but on dilution to a lower concentration the specific conductance gradually decreased with time to a minimum value attained after about 18 hours. Further dilution again produced unstable solutions but in the region of 8×10^{-5}N conductances again decreased with time to the " true " conductance minimum, and in still more dilute solutions a constant value of the specific conductance was observed within the usual time required for the establishment of thermal equilibrium inside the conductance cell.

On the concentrated side of the conductance minimum in the range of decreasing equivalent conductance a slow chemical reaction proceeds, and on the dilute side the curve represents a new, and weaker, electrolyte. In concentrated solution, compound (VII) ionises to the strong electrolyte, (VIIa), which will mask the effect of a weaker electrolyte of class (i) or (ii). However, at high dilution the degree of dissociation of both weak and strong electrolytes will become comparable and the conversion of (VIIa) into some other ionic species will be possible. Such an interconversion depends upon two isomeric ionic compounds' having a common covalent form, in this case the co-ordination compound; substances (VII) and (II) which could not form covalent molecules are stable throughout the concentration range under investigation.

EXPERIMENTAL

The infrared spectra were recorded by Mr. P. Cook of this Department, using a Grubb–Parsons model G.S.2A spectrometer. All pure materials and solutions used in the conductance measurements were handled exclusively by rigid dry-box techniques.

10-Chloro-9-oxa-10-bora-anthracene.—10-Hydroxy-9-oxa-10-bora-anthracene [4] (15 g., 1 mol.) and phosphorus pentachloride (15 g., 1 mol.) were heated under reflux for 24 hr. at 145°, after which phosphorus oxychloride was removed by distillation at the water-pump. The distillation was continued at a high-vacuum and *10-chloro-9-oxa-10-bora-anthracene* distilled as a low-melting solid which was redistilled before use, b. p. 108°/0·14 mm. (14·8 g., 90%) (Found: Cl, 16·3. $C_{12}H_8BClO$ requires Cl, 16·6%). The compound is hydrolysed with extreme rapidity in moist air with formation of the corresponding hydroxide, m. p. 285° not depressed on admixture with 10-hydroxy-9-oxa-10-bora-anthracene.

BB-*2,2′-Bipyridyl-9-oxa-10-boronia-anthracene Perchlorate.*—Equimolar amounts of 10-chloro-9-oxa-10-bora-anthracene (0·839 g.) and silver perchlorate (0·813 g.) were each dissolved in 10 ml. of dry nitromethane and then mixed. Precipitation of silver chloride was instantaneous (0·561 g., 99·5%). The colourless solution was filtered into nitromethane (5 ml.) containing 2,2′-bipyridyl (0·611 g., 1·0 mol.), and the resulting bright yellow solution was poured rapidly into dry ether which caused decolorisation and precipitation of BB-*2,2′-bipyridyl-9-oxa-10-boronia-anthracene perchlorate*. The compound was recrystallised from nitromethane–ether as white leaflets which were dried at 60°/0·1 mm. (1·110 g., 65%) (Found: C, 60·7; H, 3·4; ClO_4, 22·1; N, 6·3. $C_{22}H_{16}BClN_2O_5$ requires C, 60·75; H, 3·7; ClO_4, 22·8; N, 6·45%). The above preparation follows closely that of the corresponding 2,2′-bipyridyldiphenylboronium salt, and

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[7] Walden, *Z. phys. Chem.*, 1930, **147**, 1.

this general method was also used in the attempts to isolate a salt derived from monodentate amines (I and IV). In general, the 2,2′-bipyridyl was replaced by a tertiary aliphatic amine and the silver salts indicated in the discussion were used. No ether-insoluble salt could be isolated.

2,2′-Bipyridyldiphenylboronium Chloride.—To chlorodiphenylborane (0·290 g., 1·0 mol.) in nitrobenzene (15 ml.) was added 2,2′-bipyridyl (0·226 g., 1·0 mol.) in nitrobenzene (15 ml.). The reaction was exothermic and the solution was allowed to cool within the dry-box. During 24 hr. *2,2′-bipyridyldiphenylboronium chloride* crystallised as colourless prisms (0·4 g., 78%), m. p. 329°, which were collected on a glass filter-disc and washed with ether before being dried at 60°/0·1 mm. The concentration of a saturated solution in nitrobenzene at 15° was estimated from the specific conductance to be about 0·05N (Found: C, 74·6; H, 5·9; Cl, 10·2; N, 7·7. $C_{22}H_{18}BClN_2$ requires C, 74·2; H, 5·1; Cl, 10·0; N, 7·9%).

2,2′-Bipyridyldiphenylboronium Dichlorodiphenylborate.—Chlorodiphenylborane (0·760 g., 1 mol.), dissolved in light petroleum (20 ml.), was treated dropwise during 5 min. with 2,2′-bipyridyl (0·291 g., 0·5 mol.) dissolved in a minimum quantity of benzene. *2,2′-Bipyridyldiphenylboronium dichlorodiphenylborate* separated as a bulky white solid which was filtered off and washed once with light petroleum (yield, 0·96 g., 92·5%) (Found: Cl, 12·4; N. 4·9. $C_{54}H_{28}N_2B_2Cl_2$ requires Cl, 12·7; N, 5·0%).

Spectra.—The infrared spectra of the solid complexes of 2,2′-bipyridyl were recorded over the wavelength range 2·5—15·0 μ for pastes prepared in Nujol:

2,2′-Bipyridyldiphenylboronium perchlorate. 3·29m, 6·15s, 6·36w, 6·72m, 7·60s, 7·95m, 8·27w, 8·36m, 8·57w, 8·65w, 8·80w, 8·90m, 9·11vvs, 9·22vvs, 9·32vvs, 9·70m, 9·99w, 10·30w, 11·07w, 11·14m, 11·36m, 11·68w, 11·97w, 12·30m, 12·92vs, 13·06s, 13·28m, 13·60vs, 13·80vs, 14·20vs.

BB-2,2′-Bipyridyl-9-oxa-10-boronia-anthracene perchlorate. 3·22m, 3·25m, 5·14w, 5·36w, 5·54w, 5·79w, 5·88w, 6·01w, 6·13vs, 6·60w, 6·26s, 6·31m, 6·40m, 6·50w, 6·61m, 6·87vvs, 6·92vvs, 7·00vvs, 7·27vs, 7·41m, 7·60s, 7·68vvs, 7·75vvs, 7·92m, 8·19vvs, 8·35m, 8·57s, 8·71vs, 9·22vvs, 9·66m, 9·70m, 9·89m, 10·13w, 10·32m, 10·48w, 10·60w, 10·99s, 11·19m, 11·63m, 11·71sh, 12·14w, 12·40m, 12·71s, 13·00vvs, 13·27vvs, 13·80vs, 13·95s.

2,2′-Bipyridyldiphenylboronium chloride. 3·29m, 6·00m, 6·15s, 6·25w, 6·49w, 6·63m, 7·60s, 7·96m, 8·36s, 8·65s, 8·91m, 9·26m, 11·32m, 11·46m, 12·35m, 12·75s, 12·99s, 13·39s, 13·60vs, 13·81vvs, 14·21vs.

2,2′-Bipyridyldiphenylboronium dichlorodiphenylborate. 3·29m, 6·15m, 6·38w, 6·51m, 6·64w, 7·42s, 7·60s, 7·88m, 7·97m, 8·35s, 8·69m, 8·91m, 9·30s, 9·72m, 10·00w, 11·30m, 11·50m, 11·73m, 12·30m, 12·91vs, 13·39s, 13·56vs, 13·73s, 14·19vvs.

Conductances.—Equivalent conductance data were obtained for solutions in dry nitrobenzene by the dry-box technique described in Part I. The measurements (see Table) were carried out at 15·00° ± 0·01°.

2,2′-Bipyridyldiphenylboronium perchlorate.

10^4c	81·7	62·0	33·5	30·8	10·1	7·26	2·04	0·481
Λ	19·7	20·7	22·3	22·5	24·0	24·5	25·3	26·3

2,2′-Bipyridyldiphenylboronium chloride.

10^4c	45·1	21·1	11·1	9·78	8·17	5·11	3·02
Λ	15·1	17·7	18·8	18·9	19·3	19·0	15·5
10^4c	2·43	1·75	1·24	0·735	0·455	0·408	0·236
Λ	14·7	13·3	9·39	8·76	11·6	12·4	14·4

2,2′-Bipyridyldiphenylboronium dichlorodiphenylborate.

10^4c	134	55·4	28·6	18·3	10·2	6·19	3·94	3·12	2·30	1·32	0·837	0·361
Λ	13·8	18·3	21·6	22·3	22·8	23·4	23·5	23·6	22·2	20·2	17·3	18·6

BB-2,2′-Bipyridyl-9-oxa-10-boronia-anthracene perchlorate.

10^4c	121	43·9	20·5	9·61	4·61	1·78	0·670
Λ	18·4	21·8	23·5	24·4	25·1	26·0	26·3

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