POTENTIAL USES OF METALLOCARBORANE SANDWICH ANIONS FOR ANALYSIS, CHARACTERIZATION AND ISOLATION OF VARIOUS CATIONS AND ORGANIC BASES

Jaromír Plešek, Karel Baše, František Mareš, František Hanousek, Bohumil Štíbr and Stanislav Heřmánek

Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 250 68 Řež

Received November 10th, 1983

Unique properties of metallocarborane sandwich anions of the type $[(C_2B_9H_{11})_2M(III)]^-$ as chemical stability, specific reactivity, very strong acidity of conjugated acids along with an extreme organophility of their salts and a very limited solubility of the salts with organic cations in water are discussed. The application of metallocarboranes to analysis, characterization and isolation of organic bases, including alkaloids, amino acids, amides, *etc.*, from very diluted water solutions is suggested and demonstrated on some examples.

Borane compounds comprise many anions of very unique behavior. Among the most interesting ones belong anions of the general formula $[M(III)(C_2B_9H_{11})_2]^-$ (*I*) (M = Fe, Ia; Co, Ib; Ni, Ic) which have, beside other, several outstanding properties: *1*) great stability (thermal, redox, chemical, radiolytic), *2*) no possibility of binding proton, *i.e.* extreme acidity of the conjugate acid, *3*) ability to combine with an arbitrary cation, mostly in the form of a loose ion pair, *4*) rigid peanut-like molecule (Fig. 1) the surface of which is formed by radially pointing out H atoms; some of the hydrogen atoms are of hydridic character, which turns the anions *I* to the most hydrophobic anions ever known. The main representatives of this series are $Co(III)(C_2B_9H_{11})_2^-$ (*Ib*) and its derivatives which amalgamate high thermal, radiation, redox and chemical stability with advantageous solubilities. Due to these properties they were recognized[1,2,3] as excellent reagents for transfer of many cations in the form of loose pairs from water into water-immiscible organic solvents. In more than thirty papers and patent applications, the extraction, isolation and mutual separation of cations according to the ionic charge (extractability: $M^+ > M^{2+} > M^{3+} > M^{4+}$) and to the hydration ability (*e.g.* $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$) has been described up to now. The greatest goal in this field has been achieved in an almost quantitative separation of $^{137}Cs^+ > {}^{90}Sr^{2+} > M^{3+}$ present in the long-time cooled fission products[4,5]. In this case, the chlorinated anions have proved to be outstandingly stable and survived without serious damage the extreme radiation of radionuclides. Of a great importance is also the extreme acidity of conjugated acids of *I*, which allows

to extract individual cations from up to 3M-HNO_3 with *Ib* and up to 5M-HNO_3 with $Co(Cl_3C_2B_9H_8)_2^-$.

In this paper another exploitation of these properties is described, namely the preparation of conjugated acids and the transformation of weak bases into stable salts containing the anions $M(C_2B_9H_{11})_2^-$. In the context, preparations, stabilities in diverse media, methods of detection of *I* and also the behavior of the salts composed of *I* and of diverse metal cations will be mentioned.

Preparation, Stabilities and Characteristics of the I *Anions*

Metallocarborane sandwich anions *Ia*–*Ic* can be obtained by the original method[6,7] or more conveniently by its modification[8] according to the scheme:

$$1,2\text{-}C_2B_{10}H_{12} \xrightarrow[CH_3OH]{KOH} 7,8\text{-}C_2B_9H_{12}^- \xrightarrow[H_2O]{M^{2+},KOH} [M(III)(C_2B_9H_{11})_2]_2^- + M^\circ$$

Despite the hydridic character of some B-bonded H atoms, the *Ia*–*Ic* anions have been found to be thermally[3] (>225, 360, 225°C) and redox stable, which holds especially for *Ib* that can be oxidized or reduced only under forced conditions (Table I). It is the consequence of the closed electron shell around the Co atom and of the most stable *closo*-structure[9,10] of the CoC_2B_9 icosahedral unit with 26 electrons, *i.e.* with the most delocalized $2n + 2$ skeletal-bonding electron system. Reasons

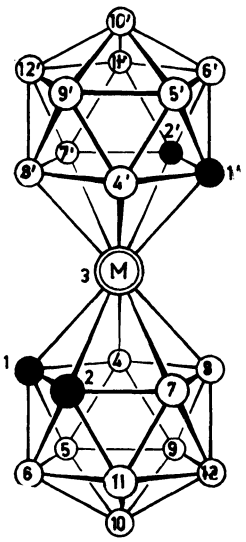


FIG. 1
Structure of anions *I* and *II*. ○ BH, ● CH, ⓪ M

for a surprising resistance of the $Fe(III)(C_2B_9H_{11})_2^-$ anion towards reduction which allows practical application of the *Ia* anion as reagent, are discussed elsewhere. On the other hand, a high stabilizing power of the $C_2B_9H_{11}^{2-}$ ligand allows easy oxidation of *Ic* to the uncharged $Ni(IV)(C_2B_9H_{11})_2$ species, which proceeds by almost any oxidizer inclusive of air and makes *Ic* applicable only under special conditions.

TABLE I
Characteristics of *Ia*–*Ic* salts

Characteristic	*Ia*	*Ib*	*Ic*
m.p. (dec) °C (ref.[3])	(>300)[a]	(>300)[a]	(>300)[a]
^1H NMR δ CH[b] carborane	—	3·89[a]	—
^{13}C δ[b]	630[c] (ref.[11])	51·2[a]	
^{11}B[b] $B_{(8)}$	−452[c] (ref.[11])	6·4[a]	−452[c,d] (4) (ref.[11])
δ (int.) $B_{(10)}$	− 30	1·1	−24[d] (1)
$B_{(5,11)}$	− 0·5	− 5·6	10[d] (2)
$B_{(9,12)}$	21	− 6·2	17[d] (2)
$B_{(4,7)}$	−402	−17·4	
$B_{(6)}$	104	−23·0	
Electronic spect.[8]	[c]- CH_3CN	[a]; CH_3OH	[c]; CH_3CN
λ, (ε)	272 (21 200)	216 (36 300)	237 (8 580)
	296 (18 000)	293 (45 000)	337 (21 400)
	444 (585)	345 sh (2 200)	435 sh (3 600)
	520 sh (400)	445 (400)	
IR cm^{-1}, Nujol mull[8]	[c] 2 552 s, 1 205 w	[a] 2 595 s, 2 517 s,	[c] 3 037 w, 2 527 s,
	1 142 w, 1 100 w,	1 223 m, 1 203 w,	1 245 m, 1 260 m,
	1 095 m, 1 068 w,	1 190 w, 1 130 w,	1 098 s, 1 063 w,
	1 018 m, 995 w,	1 100 s, 1 088 m,	1 047 m, 997 s,
	977 s, 946 s,	1 050 m, 1 010 m,	968 s, 924 m, 893 w,
	918 w, 748 w,	978 s, 933 w	872 w, 783 w,
	645 w		755 m, 743 m
$E_{1/2}$, V CH_3CN[8,f]	$d^6 \rightarrow d^5$ −0·42[c]	$d^5 \rightarrow d^6$ 1·57[c]	
		$d^6 \rightarrow d^7$ −1·46[c]	$d^6 \rightarrow d^7$ 0·25[c]
		(ref.[12]) −1·38[e]	
		$d^7 \rightarrow d^8$ −2·38[e,g]	$d^7 \rightarrow d^8$ −0·59[e,g]

[a] Cs^+; [b] in hexadeuterioacetone; [c] $N(CH_3)_4^+$; [d] unassigned; [e] $N(C_2H_5)_4^+$; [f] cyclic voltametry in 1,2-dimethoxyethane; [g] ref.[12].

The chemical stability of anions *I* under diverse conditions is remarkable. If certain redox reactions are avoided, the anions withstand boiling with 5 mol l^{-1} non-oxidizing acids as well as with up to 30% alkali hydroxides for many hours without any change. A hydridic character of $B_{(8,8')}$—H vertices becomes, however, evident under strongly acidic conditions (conc. H_2SO_4, $AlCl_3$) in the presence of compounds which are able to accept the H^- anion, after which the present nucleophilic particle enters subsequently the formed vacant B orbital. Due to this course the reaction has been called, "the nucleophillic substitution under electrophilic conditions"[11-13]. Where it is possible an intramolecular bridge is formed between the $B_{(8)}$ and $B_{(8')}$ atoms. The formation of an one-atom bridge was observed in the reaction with aqueous formaldehyde[14,15], with selenous and tellurous acid[14] as well as with nitric oxide[14] or sulfur[16] in anhydrous medium. A two-atom bridge was obtained with benzene[16] over $AlCl_3$ and three-membered bridges resulted[17] with CS_2 or acetahydride over $AlCl_3$.

Halogens, on the other hand, react instantaneously both in aqueous solutions[8,18] and in organic solvents occupying successively $B_{(8)} \gg B_{(8')} > B_{(9)} > B_{(9')} > B_{12} > > B_{(12')}$ positions[19]. Due to these differences all products from mono- to hexachloro Co-sandwiches can be isolated[19]. Halogenated compounds have been also obtained from *Ib* in highly halogenated solvents (CCl_4, $CHBr_3$) under the influence of gamma radiation[19]. Whereas anions *I* withstand boiling with up to 30% alkali hydroxides, higher concentrations and, especially, the presence of methanol cause a degradation to the $(C_2B_8H_{10}—M—C_2B_9H_{11})^{3-}$ anions[20].

With occupied $B_{(8,8')}$ and, eventually, $B_{(9,9',12,12')}$ positions the chemical stability of anions *I* rises very sharply. The conjugated acids of hexachloro or hexabromo derivatives of *Ib* withstand, for instance, contact with approx. 10M-HNO_3 without any change for many weeks, whereas the unsubstituted *Ib*/conjugated acid decomposes in contact with 5M-HNO_3 during short time[21].

The anions $M(C_2B_9H_{11})_2^-$ show several characteristics which can be used for their detection. The most important ones are absorptions in UV and in visible regions (*Ia* red, *Ib* yellow, $Co(Br_3C_2B_9H_8)_2^-$ (*II*) orange, *Ic* brown-green) and presence of a CH signal in ^1H NMR spectra (Table I). Though ^1H NMR spectroscopy failes with anions *Ia* and *Ic* which are paramagnetic, its use with diamagnetic anions *Ib* is of great importance since a strong CH carborane signal (of intensity 4 due to 4 equivalent CH vertices) makes possible its quantitative comparison with the number of H atoms (if any) present in the cation and, especially, in its solvation sphere.

As shown above the most applicable anions are those containing the central cobalt atom. Somewhat lower stability of *Ia* and *Ic* anions can be, however, surpassed by other properties such as deeper color, lower price, ESR activity, easy transfer of electrons, which can make advantage of their use.

Conjugated Acids to the Anions I

As indicated above anions $M(C_2B_9H_{11})_2^-$ cannot accommodate the loose proton, *i.e.* they do not behave as basic particles. The corresponding acids exist therefore only in the form of the I/LH^+ pair, *i.e.* in the form of $I/$conjugated acid with protons bound to the most basic molecules L in the system.

In the one-solvent system in which the solvent acts simultaneously as a base L the solubility of the I/L_nH^+ conjugated pair is, due to the similarity of L and L_nH^+, almost unlimited. This holds, for instance, for systems with L = water, alcohol, ether, ketone, ester, dimethyl sulfoxide, amine, amide, *etc.* In the two-solvent L/L′ system (L′ = more basic species) an equilibrium establishes in which the L'_nH^+ cation predominates. The solubility of the I/L'_nH^+ conjugated pair depends then on the ratio, mutual miscibility and character of both solvents. In the presence of excess L′ which is miscible with L the I/L'_nH^+ pair dissolves in L′ and, consequently, in the whole two-solvent system. This is the case of water–ethanol or water–acetone mixtures in which the conjugated I/L'_nH^+ pairs are well soluble. In an immiscible nitrobenzene(L)–water(L′) system, in which the hydroxonium $I/(H_2O)_nH^+$ salt prevails, the solubility is result of a contest of two main features: the hydrophility of the cation $(H_2O)_nH^+$ and the hydrophobity of the anion *I*. The latter property is also the reason, why the hydroxonium $I/(H_2O)_nH^+$ salt, excellently soluble in water, can be successively extracted into nitrobenzene.

Combination of a strong interaction between L'_nH^+ and L′, and of a high organophility/hydrophobity of *I* determines the result of the extraction of the *I* anions from strongly acidic aqueous solutions into diethyl ether (L′) which proceeds almost quantitatively with the smallest amount of diethyl ether still able to form a separate layer. This phenomenon can be used in practice both for preparation of the I/L'_nH^+ conjugated pairs and for recovery of the *I* anions in extraction processes.

In water, many I/L'_nH^+ conjugated pairs with L′ = organic base stronger than H_2O are sparingly soluble, which allows to use water conjugated $I/(H_2O)_nH^+$ pairs as reagents for precipitation of these bases. The solubility of the formed $I/L'H^+$ salts sharply decreases with increasing length of the alkyl groups and with increasing number of alkyls per one nitrogen atom in the base L′. Even salts formed from triethanolamine, 1,2-diaminoethane and dimethyl sulfoxide are sparingly soluble in water (Table II). Quite insoluble are the salts of natural diamino acids, whereas the salts of monoamino acids dissolve easily, inclusive of phenylalanine and tryptophan salts. But even some monoamino acids are precipitated by the aqueous solution of $Co(Br_3C_2B_9H_8)_2^-(H_2O)_nH^+$.

All the discussed L_nH^+ salts are stable only in acidic or neutral medium. With alkali hydroxides or carbonates, the bases are set free and a water solution of an alkali I/M^+ salt is recovered.

Hydrolytically Stable Amidium Salts of Ib

Reaction of the $Ib/(H_2O)_nH^+$ reagent with two molecules of amides in water gives quantitatively amidium salts[22]

$$2\ RCONR'_2 + Ib/(H_2O)_nH^+ = (RCONR'_2)_2H^+/Ib + n\ H_2O$$

TABLE II

Approximate solubilities (mol . l^{-1}) of some salts in water at ambient temperature

Cation	*Ia*	*Ib*	*II*
Cs^+	$2 . 10^{-3}$	10^{-3}	$3 . 10^{-4}$
Ag^+	[a]	$2 . 10^{-5}$	[a]
$Zn[(CH_2NH_2)_2]_2$	$< 10^{-5}$	$< 10^{-5}$	[a]
$N(CH_3)_4^+$	$2 . 10^{-5}$	$2 . 10^{-5}$	[a]
$(CH_3)_3NH^+$	[a]	$2 . 10^{-5}$	[a]
$(CH_3)_3CNH_3^+$	$3 . 10^{-4}$	$5 . 10^{-4}$	[a]
$C_5H_{10}NH_2^+$	$3 . 10^{-5}$	$8 . 10^{-5}$	10^{-5}
Urotropine.H^+	[a]	$5 . 10^{-4}$	[a]
$(HOCH_2CH_2)_3NH^+$ [b]	[a]	$5 . 10^{-4}$	$5 . 10^{-4}$
L-Arginine.H^+	[a]	$1{\cdot}5 . 10^{-3}$	10^{-4}
L-Ornithine.H^+	[a]	$2 . 10^{-3}$	[a]
L-Lysine.H^+	[a]	$2 . 10^{-3}$	[a]
Glycine.H^+	[a]	$> 10^{-1}$	$> 10^{-1}$
L-Valine.H^+	[a]	$> 10^{-1}$	[a]
L-Leucine.H^+	[a]	$> 10^{-1}$	$2 . 10^{-3}$
L-Phenylalanine.H^+	[a]	$> 5 . 10^{-2}$	10^{-3}
L-Tryptophane.H^+	[a]	$> 5 . 10^{-2}$	10^{-1}
Glucosamine.H^+	[a]	$> 10^{-1}$	$> 10^{-1}$
Cinchonine.2 H^+ [c]	[a]	10^{-6}	[a]
Ethylenediamine.2 H^+	[a]	10^{-3}	[a]
Hydrazine.2 H^+	[a]	$> 10^{-1}$	[a]
Crystal violet	[a]	$< 10^{-6}$	$< 10^{-6}$
$(CH_3)_2\overset{+}{N}HCHO$	[a]	$4{\cdot}1 . 10^{-3}$	[a]
$(CH_3)_3\overset{+}{C}NH_2COCH_3$	[a]	$2{\cdot}0 . 10^{-3}$	[a]
Caprolactam.H^+	[a]	$4{\cdot}0 . 10^{-3}$	[a]
Threshold of a color perception[d]	10^{-5}	$2 . 10^{-5}$	$3 . 10^{-5}$

[a] Not investigated combination; [b] mono- and diethanolamine salts are very soluble with *Ib* and *II*; [c] bis *Ib* salts; [d] concentration at which the color is just perceptible in a 100 mm thick layer.

which are sparingly soluble and show an outstanding hydrolytic stability, being crystallizable from hot water with the addition, if need be, of a polar water soluble organic solvent, *e.g.* ethanol.

The insoluble salts are formed especially with acyl derivatives of such amines which also form insoluble salts with *Ib*/$(H_2O)_nH^+$. These are mainly N-acyl derivatives of primary amines with an alkyl group higher than ethyl and N-acyl derivatives of all dialkylamines. The acyl group is arbitrary, *e.g.* formyl, acetyl, benzoyl. Typical examples of salt-forming amides are given in Table II.

Amidium salts derived from *Ib* precipitate in acidic medium, and their solubility ranges from 10^{-2} to 10^{-5} mol l^{-1}. They are well soluble in polar solvents as alcohols, ethers, ketones, esters, nitriles or nitro compounds. In the presence of alkali hydroxides or carbonates they disproportionate forming parent amide and a salt of the metalloborane anion and alkali cation.

The *I*/amidium salts can be titrated as free acids and they can be used for the constitution studies of amidium cations. As colored compounds, they can be also followed colorimetrically.

Being more stable than most other known amidium salts, the *Ib*/amidium salts can be used in the isolation, analysis and characterization of amides or lactams.

Solubility of Salts of the Anion I *in Water and Organic Solvents*

Comparison of salts in which the cation is paired either with anion derived from a strong inorganic acid or with the anion *I* indicates that *I*/salts exhibit unexpected differences in solubilities. This holds, for instance, for cesium and tetraalkylammonium salts which dissolve in water excellently (tens of per cents) if combined with common inorganic anions but only sparingly (fractions of one per cent) when paired with *I*. The insolubility of *I*/quaternary salts seems to be general. Similarly are insoluble also *I*/quaternary phosphonium, *I*/arsonium and *I*/tertiary sulfonium salts. All these salts are stable in acidic, neutral as well as in alkaline medium, a property which is now proposed for the isolation and separation of quaternary from tertiary ammonium salts.

The solvation of cations is very important for solubilities of the *I*/salts. The salts composed of the anion *I* and of a complexed metal cation of the type $[M(amine)_x]^{2-}$ and $[M(amine)_y]^{3-}$ are practically insoluble in water (M = Zn, Cd, Mn, Cr, Fe, Co, Ni, Cu). These salts precipitate from alkaline or neutral solutions. In acidic medium they dissolve due to decomposition of the complex cation. The precipitation of the mentioned complexed cations by *I*/salts in the presence of an appropriate amine followed by the treatment with an acid can be used as method for isolation of the particular cation.

In contrast to the above statement, the aminates of alkaline earths, inclusive of magnesium, give soluble salts with *I*. This documents how delicate differences

can significantly change the solubility. The salts composed of *I* and of well hydrated cations of any charge as Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, La^{3+} are very soluble in water. The solubilities follow a general pattern irrespective of the nature of the anion *I* the mutual replacement of which brings a small difference in solubilities amounting only to a fraction of the found values. On the other hand, the salts composed of *I* and of Cu^+, Ag^+ or Hg^+ show specific interactions between the anion and cation, which supresses their solubility in water and enhances the solubility in organic solvents.

Both water soluble and water insoluble *I*/salts dissolve easily in acetone, acetonitrile, esters and nitrocompounds. In diethyl ether and alcohols, the solubility of *I*/salts with bulky cations is limited. On the other hand, this fact is very important for crystallization of such salts. Here, alcohols–water mixtures of various concentrations are solvents of choice. The salts with very bulky organic cations dissolve readily even in chloroform or in benzene. This is, for instance, the case of the trimethyldodecylammonium but not of the tetrabutylammonium *I*/salts. The extreme organophility is very important from the practical standpoint as the quantitative composition of such solutions including *Ib* may be easily established by colorimetry or, more generally, by UV spectrometry and, especially, by ^{1}H NMR spectrometry. ^{1}H NMR shifts of diverse compounds in this series are gathered in Tables III and IV.

TABLE III

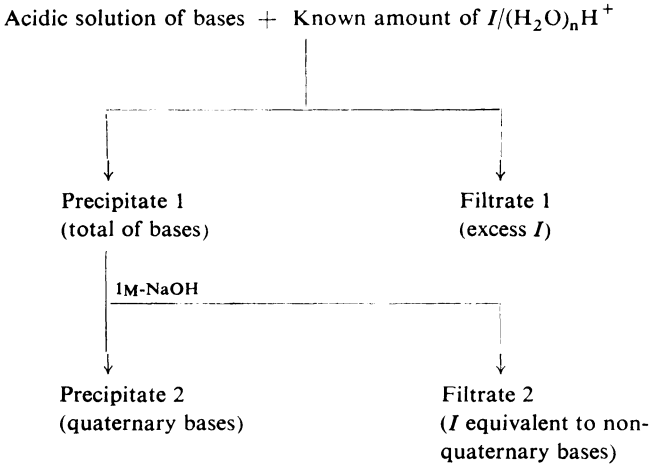
^{1}H NMR signals (δ, intensity in parentheses) of some *Ib* salts (at 60 MHz in $C^2H_3COC^2H_3$)

Cation	C—H carborane	—CH_xN	other —CH_x—	CH_3 terminal	H other
Cs^+	3·96 (4)	—	—	—	—
Ag^+	4·09 (4)	—	—	—	2·11[a] (2)
$(CH_3)_4N^+$	3·95 (4)	3·45 (12)	—	—	—
$(C_2H_5)_4N^+$	3·95 (4)	3·50 (8)	—	1·40 (12)	—
$(C_4H_9)_4N^+$	3·95 (4)	3·41[b] (8)	1·62[b] (16)	1·00 (12)	—
$(CH_3)_3NC_{12}H_{25}^+$	3·97 (4)	3·37[b] (11)	1·31[b] (20)	0·92 (3)	—
$(CH_3)_3NH^+$	3·93 (4)	3·18 (9)	—	—	—
$(CH_3)_3CNH_3^+$	3·95 (4)	—	—	1·57 (9)	—
$(CH_2)_6N_4H^+$	3·95 (4)	5·16 (12)	—	—	5·77[c] (1)
$(CH_2NH_3)_2^{2+}$	3·96 (8)	4·55[b] (4)	—	—	—

[a] H_2O associated with Ag; [b] centre of a multiplet; [c] acidic proton.

Anions I — *Reagents for Analytical Evaluation of Mixtures of Organic Bases*

The fact that *I*/water–conjugated acids precipitate both free amines and quaternary ammonium salts is now proposed for analytical evaluation of mixtures of organic bases. This test is based on the fact that *I*/salts derived from the protonized bases LH^+ are stable only in an acidic medium while the *I*/quaternary salts are stable at any pH. For a qualitative test on bulky bases (alkaloids for instance) the saturated solution of the *I*/Cs^+ salts (approxim. 0·001 mol l^{-1}) is a convenient reagent. If after acidification some drops of this reagent are added and turbidity is observed, the presence of a bulky base is highly probable.



SCHEME 1

TABLE IV

Chemical shifts of ^1H NMR signals of some *Ib* and *II* salts in different solvents at 60 MHz

Solvent	*Ib*/$(CH_3)_4N^+$		*Ib*/$(CH_3)_3NC_{12}H_{25}^+$		*II*/$(CH_3)_4N^+$	
	C—$H_{carb.}$	$(CH_3)_4N^+$	C—$H_{carb.}$	$(CH_3)_3\overset{+}{N}$—	C—$H_{carb.}$	$(CH_3)_4N^+$
$C^2H_3COC^2H_3$	3·95	3·45	3·97	3·37	4·49	3·50
C^2H_3CN	2·85	3·08	3·83	3·01	3·50	3·16
C^2HCl_3	—[a]	—[a]	3·78	3·13	—[a]	—
$C_6{}^2H_6$	—[a]	—	3·41	1·93	—[a]	—

[a] Insoluble.

The course of the analysis of a mixture of organic bases is described by the Scheme 1.

Colorimetry of the filtrate 1 establishes the anion *I* non consumed for the precipitation of the total of bases. The concentration of *I* in filtrate 2 corresponds to the molar amount of non-quaternary bases. Acetone solution of the precipitate 2 (*I*/quaternary salts) may be checked by colorimetry on the amount of quaternary bases. Other methods can be used for the investigation of the filtrate and, moreover, the particular *I*/salts can be isolated for the characterization or separation of the components. As an example, the isolation of cinchonine from a very diluted solution is described in the Experimental.

Due to the expensiveness of the anions *I* it is inevitable to recover *I* as quantitatively as possible. Several ways are possible, *e.g.* solvent extraction, adsorption on anex resins and adsorption on activated charcoal followed by re-extraction of the sorbent by organic solvent. The latter way is the method of choice for the recovery of *I* from extremely diluted water solutions. Below pH of approx. 8 anions *I* are quantitatively adsorbed on the charcoal and after saturation of the sorbent the anions are extracted by moist diethyl ether as a particular conjugated acid.

Thin Layer Chromatography of the I/*Salts*

First information on the *I*/salts can be obtained by silica gel thin layer chromatography using a mixture of acetonitrile–chloroform in various proportions as the eluent. Colored spots of *I* are visible without further treatment of the plate, but an exposition to iodine vapors may further enhance the sensitivity of the method.

TABLE V

Relative velocities of some *Ia* salts on silica gel (Silufol, CH_3CN–$CHCl_3$ 1 : 2); the velocity is related to *Ia*/$N(CH_3)_4^+$ R_F 0·38 = 100

Cation	Velocity	Cation	Velocity
$HOCH_2CH_2NH_3^+$	70	$(CH_3)_2NH_2^+$	100
$(HOCH_2CH_2)_2NH_2^+$	70	$(CH_3)_3NH^+$	100
$(HOCH_2CH_2)_3NH^+$	70	$C_6H_5NH_2^+$	100
H^+	95	$C_5H_5NH^+$	105
Na^+	95	$(C_2H_5)_3NH^+$	126
K^+	95	$(C_2H_5)_4N^+$	126
Cs^+ [a]	95	$(CH_3)_3CNH_3^+$	133
NH_4^+	95	n-$(C_4H_9)NH_3^+$	133
Ca^{2+}	95	2,4,6$(CH_3)_3C_5H_2NH^+$	133
$(CH_3)_4N^+$	100	$(C_4H_9)_4N^+$	187

[a] *Ia*, *Ib* and *II* Cs^+ salts show relative velocities 95, 73 and 109, respectively.

In several cases, the cation remains associated with the *Ib* anion during the development of the chromatogram, making some separations possible. Relative travel velocities of the *Ia*/salts are shown in the Table V and of the *Ib*/salts in the Table VI.

It is obvious that inorganic cations cannot be distinguished by this method. Somewhat better is the situation with the salts of organic bases. Relatively easy is the separation of quaternary ammonium salts according to the bulkiness of the cation and, generally, of the bulky bases from the smaller ones. The same applies to the salts of diamino acids. On the other hand, a systematic search for better solvent system may lead to a quite better separation of the *I*/salts.

EXPERIMENTAL

The ^{1}H NMR spectra were obtained with a Tesla BS 467 (60 MHz), a Varian XL-100 (100 MHz) and a Varian XL-200 (200 MHz) spectrometers. UV and visible spectra were recorded on a Beckman Acta M IV device and IR spectra on Beckman IR-20 A spectrometer. The starting *I*/Cs salts were prepared according to the aqueous method[8]. Thin-layer chromatography was performed on Silufol sheets (Kavalier, Votice, Czechoslovakia) with CH_3CN—$CHCl_3$ 1 : 2 as an eluent.

Approximate solubilities of I *salts*: In the range between 10^{-2} and $5 . 10^{-4}$ mol l^{-1}, the solubilities were estimated visually by comparative colorimetry. The saturated solutions of the substances were visually compared with standard solutions of known concentration of $I/(H_2O)_nH^+$ acids in a 50 mm layer. In the range below $5 . 10^{-4}$ mol l^{-1}, turbidimetry was used. The same proportions of very diluted solutions of the base and an equivalently diluted solution of $I/(H_2O)_n . H^+$ were mixed together and after 30 min the transparency of the mixture was investigated. As solubility limit, the lowest concentration was recorded at which still a slight opacity, disappearing when diluted to one half by water, was observed.

$M(C_2B_9H_{11})_2^- (H_2O)_nH^+$ Solutions

The mixture of 100 ml of 10% sulfuric acid and of 0·1 mol of the I/Cs^+ salt was shaken with 200 ml of diethyl ether. After 10 min the acid layer was separated (it contained all Cs^+ which can be reused), a new 50 ml portion of 10% sulfuric acid was added and shaking was repeated for 5 min. The last operation was repeated once more. To the colored ether layer, 100 ml of water

TABLE VI

Relative velocities of some *Ib* salts; the velocity is related to *Ia*/$N(CH_3)_4^+$ R_F 0·38 = 100

Cation	Velocity	Cation	Velocity
Cs^+	73	L-arginine.H^+	50
$(CH_3)_4N^+$	100	L-ornithine.H^+	66
$(C_2H_5)_4N^+$	137	L-lysine.H^+	69
$(C_4H_9)_4N^+$	198	cinchonine.2 H^+	158
$(CH_3)_3CNH_3^+$	126		

was added and diethyl ether was evaporated *in vacuo* until a clear water solution remained: approx. 50 ml of water was distilled off with last traces of diethyl ether and the remaining solution was diluted with water to 100 ml. Essentially a quantitative yield of the $I/(H_2O)_nH^+$ solution (0·1 mol l^{-1}) was obtained. The $I/(H_2O)_nH^+$ solutions are stable for many months. By the same technique, *I*/conjugated acids can be obtained starting with almost any salt, inclusive of quaternary ammonium salts.

Salts of *I*

Water soluble salts were prepared by neutralization of the $I/(H_2O)_nH^+$ acids with metal hydroxides, carbonates, oxides or salts of weak organic acids. In water instead of a simple neutralization, the ethereal solution of $I/(H_2O)_nH^+$ could also be neutralized with aqueous solution or suspension of an equivalent of the above mentioned metal derivatives. After the evaporation of the ether, aqueous solution of the salt remained.

Non-quaternary salts sparingly soluble in water, mentioned in Tables II—VI, were prepared by the neutralization of 0·01 mol l^{-1} solutions of the bases by an equivalent amount of the $I/(H_2O)_nH^+$ acid.

Ia/$(CH_3)_3CNH_3^+$ *salt*: To the solution of 0·75 g of t-butylamine in 50 ml of water, 60 ml of 0·2 mol l^{-1} *Ia*/$(H_2O)_nH^+$ aqueous solution was added, the suspension was heated to 80°C, about 30 ml of ethanol was added and the hot solution was filtered and left to cool overnight. The product was sucked off, washed with three 10 ml portions of 30% ethanol and dried in air; 4·4 g (78%) of red leaflets were obtained. For *Ia*/$(CH_3)_3CNH_3^+$ calculated: 18·5%, found: 18·3% of $(CH_3)_3CNH_2$ (distillation method).

Ia/L-*ornithine salt*: To the solution of 1·7 g of L-ornithine. HCl (0·01 mol) in 100 ml of water, 55 ml of 0·2 mol l^{-1} *Ib*/$(H_2O)_nH^+$ acid was added. The precipitate was dissolved by heating to 80°C and after filtration, the solution was set aside for 4 h. Needles were separated by suction, washed with three 10 ml portions of water and dried in air (4·8 g, 95%). The ^{1}H NMR spectrum confirmed the 1 : 1 *Ib*/ornithin.H^+ ratio, showing C—H_{carb} at 5·35 ppm (4), CH_2 at 3·91 ppm (4) and 2·25 ppm (2), and the methine CH signal at 4·42 ppm (1). The signals of the NH_3^+ protons as well as that of the —COOH group were not observed.

Quaternary salts: A hot solution of 4·6 g (0·01 mol) of *Ib*/Cs^+ in 30 ml of 75% ethanol was was poured into a hot solution of 3·7 g (0·01 mol) of $(C_4H_9)_4N^+I^-$ in 50 ml of 75% ethanol and the resulting mixture was left to cool down. After several seconds, the yellow needles of the salt began to separate. After 4 h, the product was sucked off, washed with two 20 ml portions of 75% ethanol and dried in air for 24 h at an ambient temperature, yielding 6·7 g (97%) of *Ib*/ /$(C_4H_9)_4N^+$. According to the ^{1}H NMR spectrum (Table III) no water or ethanol were present.

Ib/Ag^+ *salt*: To the solution of 1·7 g (0·01 mol) of $AgNO_3$ in 50 ml of water, 50 ml of 0·2 mol . . l^{-1} aqueous solution of *Ib*/$(H_2O)_nH^+$ was added. The precipitate was heated to approx. 40°C and acetone was added just to dissolve all solid material. After standing overnight, the yellow product was sucked off and dried *in vacuo* of 1·3 kPa at room temperature for 4 h and then at ambient temperature in air for 24 h, yielding 5·4 g, 96% of *Ib*/Ag^+ which according to the ^{1}H NMR contained one mol of water.

In the same way, the *Ia*/Ag^+ salt was prepared for the IR investigation. The *Ia*/Cu^+ and *Ib*/Cu^+ salts were obtained by a metathesis of Cu_2Cl_2 with an equivalent amount of the appropriate *I*/Cs^+ salt in acetone, followed by the filtration of the insoluble CsCl, dilution of the filtrate with an equal volume of water and evaporation of a part of acetone *in vacuo*. The crystallization of the precipitate was performed as above with the Ag^+ salt. According to IR, the Ag^+, Cu^+ and Hg^+ salts show a tight-pair character[3].

Oxidation of $Fe(II)(C_2B_9H_{11})_2^{2-}$ to $Fe(III)(C_2B_9H_{11})_2^{-}$ by $CuCl_2$

To the hot solution of 3·0 g (0·005 mol) of $Fe(II)(C_2B_9H_{11})_2Cs_2$ in 50 ml of 20% ethanol, a solution of $CuCl_2.2\,H_2O$ (0·85 g, 0·005 mol) in 20 ml of 20% ethanol was added. The red solution turned immediately to a red-violet one and a white precipitate appeared. After the filtration, the solution was set aside overnight. Black needles of the *Ia*/Cs^+ salt (2·0 g, 88%) separated. They were pure according to the electronic spectra in acetonitrile. The white precipitate was washed with degassed water until the filtrate was colorless and then with two 5 ml portions of acetone, yielding after drying *in vacuo* 0·45 g (91%) of Cu_2Cl_2.

Iodination of *Ib*/Cs^+

A solution of *Ib*/Cs^+ (2·3 g, 0·005 mol) and of iodine (5·1 g, 0·04 mol) in 50 ml of acetic acid was heated in a boiling water bath for 4 h. The brown solution was diluted with 50 ml of water and enough Na_2SO_3 was added to reduce the excess iodine. The resulting orange solution was diluted with further 100 ml of water and was set aside overnight. The product was sucked off, washed with three 10 ml portions of water and crystallized from hot 30% ethanol, yielding orange needles of $Co(8\text{-}IC_2B_9H_{10})_2Cs^+$ (3·0 g, 85%). The ^1H NMR showed one $CH_{carborane}$ signal at 4·43 ppm, the ^{11}B NMR spectrum exhibited five signals: 2·8 d (1), −3·3 d (4), −5·1 s (1), −17·0 d (2) and −22·6 d (1) ppm: related to $BF_3.O(C_2H_5)_2$ reading upfield; s singlet, d doublet, (intensity)).

Estimation of the Total Base Content and of the Quaternary: Non-Quaternary Bases Ratio

To 500 ml of aqueous solution, containing 1 mmol of $(CH_3)_4NCl$ and 1 mmol of $(CH_3)_3NHCl$, 20 ml of 0·2 mol l^{-1} aqueous solution of *Ib*/$(H_2O)_nH^+$ was added under stirring and the mixture was set aside overnight. The precipitate was collected on filter, washed with 3 × 20 ml of water, the filtrates were diluted to 600 ml and the excess of 2·05 mmol of the *Ib*/$(H_2O)_nH^+$ was estimated colorimetrically at 445 nm. Thus 1·95 mmol (97·7%) of the *Ib*/$(H_2O)_nH^+$ was consummed for the total base content. The precipitate was washed down quantitatively into 50 ml of 1M-NaOH and the suspension was stirred for 30 min. After collecting the solid substance on filter, and washing with 3 × 20 ml of water, the combined filtrates were diluted to 200 ml and 1·04 mmol of the *Ib* anion was found colorimetrically in the water solution. This corresponded to 104% of the theoretically expected content of the non-quaternary base. The insoluble yellow material was washed with 2 × 5 ml of ethanol and dried in air yielding 0·37 g (96·6%) of *Ib*/$(CH_3)_4N^+$ which was found to be pure according to the ^1H NMR, showing 1 : 3·02 ratio of CH_{carb} : $(CH_3)_4N$ signals, *i.e.* 4 : 12·08 for protons. No crystal water was present. Apparently, some losses occurred in this analysis which should be much less with bulkier bases.

Isolation of Cinchonine

To the aqueous solution of 0·10 g (0·34 mmol) of cinchonine neutralized with 3·6 ml of 0·2M-HCl and filled up with water to 1 000 ml were added 5·0 ml of a 0·2 mol l^{-1} *Ib*/$(H_2O)_nH^+$ aqueous solution, the turbid solution was heated to 50°C and set aside overnight. The precipitate was collected on filter, washed with 3 × 20 ml portions of water, dissolved gradually in a total volume of 50 ml of acetone and filtered into 100 ml of ethanol. Acetone and about 80 ml of ethanol were evaporated *in vacuo*, the remainder was diluted with an identical volume of water, heated to boil and set aside overnight. The yellow leaflets of *Ib*/cinchonine.H^+ (0·28 g, 87·5%) were filtered off and dried *in vacuo*. The yellow ethanolic parent liquor contained still some quantity

of this compound, but it was not worked up further. The relative RR_F of *Ib*/cinchonine.H^+ was found to be 216, in comparison with $RR_F = 100$ of *Ib*/$(CH_3)_4N^+$ ($R_F = 0{\cdot}26$) in CH_3CN—$CHCl_3$ 1 : 2. Solubility of *Ib*/cinchonine.H^+ (water): 10^{-6} mol l^{-1} (by turbidimetry).

REFERENCES

1. Kyrš M., Heřmánek S., Rais J., Plešek J.: Czech. 182 913 (23. 12. 1977).
2. Kyrš M., Rais J., Selucký P., Škarda V., Heřmánek S., Plešek J., Koryta J., Jänchenová H.: 3rd International Meeting on Boron Chemistry, Abstr. No 14, July 5—9, 1976, München and Ettal, FRG.
3. Heřmánek S., Plešek J., Baše K., Štíbr B., Mareš F., Hanousek F.: Unpublished results.
4. Kyrš M., Kadlecová L., Rais J., Selucký P., Teplý J., Galkin Ya. B., Lyubcev R. F., Rovnyi S. I., Romanovskii V. N., Tichonov N. S., Shishkin D. N.: Proceedings of the IV. Symposium SEV, Vol. *1*, 246, March 28th, 1977, Karlovy Vary, Czechoslovakia; Paper KV 77/T5, Czechoslovak Atomic Energy Commision, Prague 1977.
5. Selucký P., Vaňura R., Rais J., Kyrš M.: Radiochem. Radioanal. Lett. *38*, 297 (1979).
6. Hawthorne M. F., Andrews T. D.: J. Chem. Soc., Chem. Commun. *19*, 443 (1965).
7. Hawthorne M. F., Young D. C., Wegner P. A.: J. Amer. Chem. Soc. *87*, 1818 (1965).
8. Hawthorne M. F., Young D. C., Andrews T. D., Howe D. V., Pilling R. L., Pitts A. D., Reintjes M., Warren L. F., Wegner P. A.: J. Amer. Chem. Soc. *90*, 879 (1968).
9. Wade K.: Advan. Inorg. Chem. Radiochem. *18*, 1 (1976).
10. Rudolph R.: Accounts Chem. Res. *9*, 446 (1976).
11. Wiersema R. J., Hawthorne M. F.: J. Amer. Chem. Soc. *96*, 761 (1974).
12. Geiger W. E. jr, Bowden W. L., El Murr N.: Inorg. Chem. *18*, 2358 (1979).
13. Plešek J., Baše K., Heřmánek S.: 2nd International Meeting on Boron Chemistry, Abstract No 46, March 25—29, 1974, Leeds, U.K.
14. Plešek J., Heřmánek S., Baše K., Todd L. J., Wright W. F.: This Journal *41*, 3509 (1976).
15. Janoušek Z., Plešek J., Heřmánek S., Baše K., Todd L. J., Wright W. F.: This Journal *46*, 2818 (1981).
16. Plešek J., Heřmánek S.: This Journal *43*, 1325 (1978).
17. Francis J. N., Hawthorne M. F.: Inorg. Chem. *10*, 594 (1971).
18. Selucký P., Baše K., Plešek J., Heřmánek S., Rais J.: Czech. Appl. 6892—79.
19. Mátel L., Čech R., Macášek F., Heřmánek S., Plešek J.: Polyhedron, in press.
20. Francis J. N., Hawthorne M. F.: J. Amer. Chem. Soc. *90*, 1663 (1958).
21. Mátel L., Macášek F., Kamenistá H.: Radiochem. Radioanal. Lett. *46*, 1 (1981).
22. Plešek J., Heřmánek S.: Czech. Appl. 3553—81.

Translated by the author (S. H.).