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Phosphorus-borates with low melting points

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(54) Title: PHOSPHOROUS-BORATES WITH LOW MELTING POINTS

(57) Abstract: The present invention relates to phosphorous borates, methods for their preparation and to the use of these salts in primary batteries, secondary batteries, capacitors, supercapacitors and/or galvanic cells. Furthermore, the present invention relates to the use of these salts as hydraulic liquid, conducting salt, catalyst, solvent, electrolyte or starting compound.

## Phosphorus-borates with low melting points

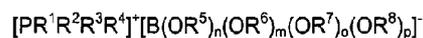
- The present invention relates to phosphorous borates, methods for their preparation and to the use of these salts in primary batteries, secondary  
5 batteries, capacitors, supercapacitors and/or galvanic cells.  
Furthermore, the present invention relates to the use of these salts as hydraulic liquid, conducting salt, catalyst, solvent, electrolyte or starting compound.
- 10 Weakly associated salts are the basis of many electrolytes. They are useful in electrochemical cells such as batteries, electronic parts such as capacitors, double layer capacitors, super or ultra capacitors as well as for organic synthesis, especially catalysis.
- 15 Solvent-free ionic liquids or "room temperature molten salts" were first disclosed in US 2,446,331. A disadvantage of these first molten salts and a serious problem with any solvent-free ionic liquid containing strong Lewis acids such as  $\text{AlCl}_3$  is the liberation of toxic gases upon exposure to moisture. Work in room temperature melts has been dominated by the use of  $\text{AlCl}_3$  and  
20 1-ethyl-3-methylimidazolium (EMI) chloride. Wilkes and Zaworotko presented new solvent-free ionic liquids in 1992, EMI  $\text{BF}_4^-$  and EMI  $\text{O}_2\text{CCH}_3^-$  (J. Chem. Soc. Commun., 1992, S. 965). However, these ionic media suffer from the same problems with moisture as previous compounds. Because  $\text{BF}_4^-$  and  $\text{CH}_3\text{CO}_2^-$  -anions oxidize at relatively low potentials, they are unsuitable for use  
25 in electrochemical cells.
- US 5,827,602 teaches ionic liquids comprising a number of heterocyclic organic cations and imides or methanides as counteranion. These ionic liquids demonstrate good conducting properties. A disadvantage of these salts lies  
30 with the costly preparation of the starting compounds, in particular the preparation of the anions.

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Accordingly, there is a need for the provision of solvent-free ionic liquids that demonstrate a broad temperature range in a molten state and at the same time are suitable for electrochemical applications and economical in their preparation.

A further problem underlying the present invention is the provision of more powerful and more stable primary and secondary batteries, capacitors, supercapacitors and galvanic cells.

This problem is solved according to the present invention by providing new salts of the general formula [I],



[I]

wherein

$\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$  denote, in each case independently of one another, a  $\text{C}_{1-20}$  linear, branched or cyclic, saturated or unsaturated aliphatic radical or a  $\text{C}_{6-20}$ -aromatic or heteroaromatic radical, wherein the aliphatic, aromatic or heteroaromatic radicals may comprise one or more ether functional groups and/or may be further substituted, preferably further substituted by at least one radical of the formula  $-\text{C}_q\text{F}_{(2q+1-x)}\text{H}_x$ , wherein  $1 \leq q \leq 6$  and  $0 \leq x \leq 2q+1$ ,

$\text{R}^5, \text{R}^6, \text{R}^7$  and  $\text{R}^8$  denote, in each case independently of one another, a  $\text{C}_{6-20}$  aromatic or heteroaromatic radical, that may be further substituted by at least one halogen-radical, preferably a F- or Cl-radical and/or at least one radical of the formula  $-\text{C}_q\text{F}_{(2q+1-x)}\text{H}_x$ , wherein  $1 \leq q \leq 6$  and  $0 \leq x \leq 2q+1$ ,

or a C<sub>1-8</sub>, linear, branched or cyclic, saturated or unsaturated, aliphatic radical, that may be further substituted by at least one halogen-radical, preferably a F- or Cl-radical and/or at least one radical of the formula

5  $-(C_qF_{(2q+1-x)}H_x)_2$ ,  $-O(C_qF_{(2q+1-x)}H_x)$ ,  $-SO_2(C_qF_{(2q+1-x)}H_x)$  or  $-C_qF_{(2q+1-x)}H_x$ , wherein  $1 \leq q \leq 6$  and  $0 \leq x \leq 2q+1$ ,

or a carboxylic-, dicarboxylic- or hydroxycarboxylic, linear, branched or cyclic, saturated or unsaturated C<sub>1-8</sub>-aliphatic or C<sub>6-20</sub>-aromatic or heteroaromatic radical that may be further substituted by at least one halogen-radical, preferably a F- or Cl-radical and/or at least one radical of the formula -

10  $N(C_qF_{(2q+1-x)}H_x)_2$ ,  $-O(C_qF_{(2q+1-x)}H_x)$ ,  $-SO_2(C_qF_{(2q+1-x)}H_x)$  or  $-C_qF_{(2q+1-x)}H_x$ , wherein  $1 \leq q \leq 6$  and  $0 \leq x \leq 2q+1$ ,

and wherein

at least two of the radicals R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> may be bound to each other by single or double bonds, and/or

15 at least two of the radicals R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> may be bound to each other by single or double bonds,

and  $0 \leq n, m, o, p \leq 4$  and  $m + n + o + p = 4$

and wherein the following salts are disclaimed:

20

Bis[salicylato(2-)]borate (III)-tetrabutylphosphonium,

Tetrakis[1-naphthalenolato (1-)]-borate-tetraphenylphosphonium,

Bis[2-hydroxybenzoato (2-)]-borate-tetrabutylphosphonium,

Bis[1,2-benzodiolato(2-), O, O']-borate-tetraphenylphosphonium,

25 Tetrabutoxy(1-)borate-tetraphenylphosphonium,

Tetrakis(1,1'-biphenyl-4,4'-diolato)-borate-tetraphenylphosphonium,

Bis[2,3-naphthalendiolato (2-) O, O']-borate-tetraphenylphosphonium.

In a preferred embodiment the present invention relates to salts wherein at

30 least two of the radicals R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> are identical and/or bound to each other by single or double bonds.

A further preferred embodiment relates to salts, wherein at least two of the radicals  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$  are identical and/or bound to each other by single or double bonds.

5

More preferred salts are those, wherein at least one of the radicals,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  denotes, in each case independently of one another, a radical selected from the group consisting of phenyl-, naphthyl-, anthracenyl, phenanthrenyl, pyridyl-, pyracyl- or pyrimidyl-radicals, that may be further substituted by at least one halogen radical, preferably a F- or Cl-radical and/or at least one radical of the formula  $-C_qF_{(2q+1-x)}H_x$ , wherein  $1 \leq q \leq 6$  and  $0 \leq x \leq 2q+1$ .

10

Further more preferred salts are those, wherein at least one of the radicals  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  denotes phenyl or  $C_{1-20}$ -alkyl, most preferably  $C_6H_{13}$ - or  $C_{14}H_{29}$ -alkyl.

15

In a most preferred embodiment the present invention relates to salts, wherein at least two of the radicals  $R^5$ ,  $R^6$ ,  $R^7$  or  $R^8$  denote a 2,2'-biphenyl-diolato(2')O,O'-, a 1,2-benzen-diolato(2-)O,O'- or a salicylato(2-)-radical.

20

Furthermore, most preferred salt are those, wherein  $[B(OR^5)_n(OR^6)_m(OR^7)_b(OR^8)_p]$  denotes bis[2,2'-biphenyl-diolato(2')O,O']-borate, bis[1,2-benzen-diolato(2-)O,O']-borate or bis[salicylato(2-)]-borate.

25

The salts of the present invention provide a number of advantages. They are not sensitive to hydrolysis. Their tendency to decompose is very small. They have a high thermal stability and they are soluble in most standard aprotic solvents, even in unpolar solvents of low viscosity such as toluene or hexane. In addition, these salts demonstrate a very large temperature range of up to several hundred degrees Celcius in which they are in a stable molten state.

30

For example,  $[P(C_6H_{13})_3C_{14}H_{29}][B(OC(O)C_6H_4O)_2]$  is a liquid from -150 to +300°C. Therefore, these salts are suitable for a number of applications, such

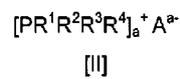
as electrochemical applications or as hydraulic liquid, or for the catalysis of organic reactions or as inert solvent for highly reactive chemicals.

They are especially useful as salts for electrolytes. Electrolytes comprising said salts are electrochemically stable, temperature and humidity resistant.

5 Also, such electrolytes demonstrate an excellent cyclic behavior and performance in electrical cells.

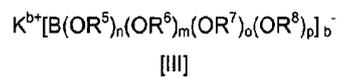
A further aspect of the present invention relates to a method for the preparation of salts, wherein a salt of the general formula [II]

10



and a salt of the general formula [III]

15



wherein

20

A<sup>-</sup> denotes an anion, a= 1 to 3, preferably a=1, more preferably an anion chosen from Cl, Br, or I,

K<sup>+</sup> denotes a cation, b= 1 to 3, preferably b=1, more preferably a cation chosen from H, Li, K, Na, Ag or NR<sub>4</sub><sup>+</sup>,

25 and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, n, m, o, p, have the meanings according to claim 1,

are dissolved in a suitable solvent and mixed and the resulting salt is isolated and/or purified.

30

Standard methods well known to those skilled in the art may be used for the

isolation and/or purification of the resulting salt.

In a preferred embodiment the resulting salt is purified by separating the byproduct  $K^+A^-$  by precipitation, ionic exchange chromatography or by  
5 evaporation, if  $K^+$  denotes hydrogen.

A number of suitable aprotic solvents are available for the preparation of the salts, such as, for example, esters, ethers, carbonates, nitriles, sulfonic acid esters, toluene, methylenechloride,  $CHCl_3$ .  
10

Preferred suitable solvents are acetonitrile, THF (tetrahydrofuran) or a mixture of at least two of these solvents.

More preferred suitable solvent are aprotic solvents, preferably acetonitrile or  
15 THF (tetrahydrofuran) or a mixture of at least two aprotic solvents, wherein the resulting salt  $K^+A^-$  is insoluble.

A preferred temperature range for mixing the salts of formula [II] and [III] is 0 to 100°C, more preferably 0 to 50°C and most preferably 10 to 40°C.  
20

In a preferred embodiment the reaction is carried out in a solvent or solvent mixture that is directly suitable for use in a secondary or primary battery, a capacitor, a supercapacitor or a galvanic cell.

25 Preferred solvents or solvent mixtures that are directly suitable for use in a secondary or primary battery, a capacitor or a galvanic cell are organic carbonates, preferably an ethylenecarbonate, propylenecarbonate, butylene-carbonate, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, methylpropylcarbonate or a mixture of at least two of these solvents.

30 The method according to the present invention provides almost pure salts in

high yield with little impurities. Often the reaction proceeds to give quantitative yields and only traces of impurities. If necessary, the salts may be further purified according to standard methods, for example, by recrystallisation in a suitable solvent or solvent mixture. A suitable solvent or solvent mixture can easily be selected by preliminary experiments.

The method for preparing the salts according to the invention is simply, efficient and without any complicated or dangerous steps.

In a further aspect, the present invention relates to the use of at least one of the salts according to the invention alone or in combination with further salts and/or additives in primary batteries, secondary batteries, capacitors, supercapacitors and/or galvanic cells.

The salts are suitable for preparing electrolytes, preferably electrolytes for primary batteries, secondary batteries, capacitors, supercapacitors and/or galvanic cells.

Such an electrolyte comprises at least one compound of the present invention. The preparation of soluble or solid electrolytes is well known to the average expert in the field of electrochemistry (for example: D. Linden, Handbook of Batteries, Second Edition, McGraw-Hill Inc., New York 1995; J. Barthel and H.-J. Gores, Solution Chemistry: A Cutting Edge in Modern Electrochemical Technology in G. Mamantov and A.I. Popov (publishers) Chemistry of Nonaqueous Solutions, Current Progress, VCH Verlagsgemeinschaft, Weinheim 1994).

Electrolytes can be prepared as a solution or a solid material. A solid electrolyte may be a polymer electrolyte optionally comprising a cross-linked polymer and at least one conducting salt or a gel electrolyte that comprises at least one solvent in addition to at least one conducting salt and an optional cross-linked polymer.

30

In a preferred embodiment, these electrolytes have a salt concentration of the electrolyte of 0,01 – 3 mol/l, preferably of 0,01 – 2 mol/l, most preferably of 0,1 – 1,5 mol/l.

- 5 Electrolytes according to the present invention provide excellent electro-chemical properties for most uses in batteries, conductors and galvanic cells. These electrolytes provide excellent conductivity as well as stability and safety.

- 10 In a further aspect of the present invention relates to primary batteries, secondary batteries, capacitors, supercapacitors and/or galvanic cells comprising at least one of the salts of the present invention.

- 15 In a further aspect of the present invention relates to a hydraulic liquid comprising at least one compound of the general formula [I].

- 20 Primary batteries, secondary batteries, capacitors, supercapacitors, galvanic cells or hydraulic liquids according to the present invention are suitable to be employed under extreme conditions such as high temperatures or high humidity without an effect on the performance or life span of the device or liquid.

- 25 In a further aspect the present invention relates to the use of a salt according to the present invention as a solvent or as a conducting salt in an electrolyte of electrochemical devices.

- 30 Preferably, salts of the present invention are used as a catalyst, solvent, electrolyte or starting compound for the preparation of organic compounds.

**Examples**

The following examples merely serve to illustrate the invention in an exemplary manner. The examples are not meant to limit the general concept of the present invention in any way.

The following abbreviations will be used below:

	BBPB	bis[2,2'-biphenyl-diolato(2'O,O')]-borate
10	BBB	bis[1,2-benzene-diolato(2-O,O)]-borate
	BSB	bis[salicylato(2-)]-borate
	C <sub>6</sub>	C <sub>6</sub> H <sub>13</sub>
	C <sub>14</sub>	C <sub>14</sub> H <sub>29</sub>

15 Example 1 Synthesis and Characterisation of [(C<sub>6</sub>)<sub>3</sub>P(C<sub>14</sub>)] [BBPB]

Both, Li[BBPB] (2.61 g, 6.75 mmol) and [(C<sub>6</sub>)<sub>3</sub>P(C<sub>14</sub>)] [Cl] (3.51g, 6.75 mmol) were each dissolved completely in 150 ml acetonitrile to give clear, colourless solutions. Upon addition of the former to the latter no change was produced initially. A fine white precipitate developed over the first several minutes of stirring. After three hours of stirring at room temperature the solution was filtered through a sintered glass funnel (#3) to give a clear, colourless filtrate. Removal of the solvent by rotavap yielded a white slurry, which was taken up in 125 ml CH<sub>2</sub>Cl<sub>2</sub>. This solution was washed repeatedly with water (5 x 300 mL) until the solution became clear and pale yellow in color. Removal of the solvent by rotavap produced a pale yellow, viscous liquid. This was heated to 100 °C under vacuum for three hours to remove any residual solvent. The total yield of product, identified as [(C<sub>6</sub>)<sub>3</sub>P(C<sub>14</sub>)] [BBPB], was 5.30 g (90%).

Example 2 Synthesis and Characterisation of  $[(C_6)_3P(C_{14})][BBB]$ 

Both  $Li[BBB]$  (1.87 g, 7.99 mmol) and  $[(C_6)_3P(C_{14})][Cl]$  (3.65 g, 7.03 mmol) were dissolved completely in 100 ml THF each to give clear, colourless solutions. These were combined in a 250 ml round-bottom flask and allowed to stir for one hour, during which time no changes were observed. The reaction mixture was then cooled in an ice-bath and 20 ml cold hexane were added, producing a hazy, white precipitate. This mixture was filtered through a sintered glass funnel (#3) and the solvent was removed by rotavap. The resulting yellow liquid was taken up in 100 ml  $CH_2Cl_2$  and washed with water repeatedly (5 x 300 ml). Removal of the solvent by rotavap yielded a clear, slightly pink liquid, which reverted to a solid after several hours at room temperature. This precipitate was heated to 100 °C under vacuum for one hour to remove any residual solvent.

Total yield of this solid, identified as  $[(C_6)_3P(C_{14})][BBB]$ , was 4.07g (5.72 mmol, 81 mol %).

- Melting point: 49 °C; (decomposition above 200 °C, no freezing point observed).
- Solubility: see table 1
- Analysis calculated for  $C_{44}H_{76}B_0P$  [%]: C, 74.34; H, 10.78; N, 0.00.
- Found: C; 74.09; H, 10.98; N, 0.00.
- $^1H$ -NMR [300 MHz,  $\delta(TMS \text{ in } CDCl_3)$ ] in  $CDCl_3$  at 25 °C:  $\delta = 6.59$  (s, 8 H, anion); 2.17-0.88 (m, 68 H, cation).
- $^{13}C$ -NMR [75.45 MHz,  $\delta(TMS \text{ in } CDCl_3)$ ] in  $CDCl_3$  at 25 °C:  $\delta = 152.06$ , 118.23, 108.94 (s, anion); 32.31-14.30 (various s, cation).
- $^{31}P$ -NMR [121.49 MHz] in  $CDCl_3$  at 25 °C:  $\delta = 30.3$ .
- $^{11}B$ -NMR [160.46 MHz,  $\delta(BF_3 \cdot OEt_2 \text{ in } D_2O)$ ] in  $D_6$ -acetone at 25 °C:  $\delta = 10.87$ .

30

Example 3                    Synthesis and Characterisation of [(C<sub>6</sub>)<sub>3</sub>P(C<sub>14</sub>)]BSB]

Both, Li[BSB] (5.75 g, 19.84 mmol) and [(C<sub>6</sub>)<sub>3</sub>P(C<sub>14</sub>)]Cl] (10.29 g, 19.81 mmol)  
 5 were dissolved with gentle heating in 75 ml acetonitrile each to give clear,  
 colourless solutions. These were combined in a 500 ml round-bottom flask.  
 No changes were observed initially, but after several seconds a white  
 precipitate developed. The reaction was allowed to stir for one hour at room  
 temperature during which time no further changes were observed. Filtration  
 10 through a sintered glass funnel (#3) gave a clear, colourless filtrate and a  
 small amount of white powder (LiCl). Removal of the solvent by from the  
 filtrate by rotavap gave a white slurry. This was taken up in 150 ml CH<sub>2</sub>Cl<sub>2</sub> and  
 washed with water repeatedly (8 x 300 ml), producing a clear, faintly yellow  
 liquid. Removal of the solvent by rotavap yielded a clear, colourless oil, which  
 15 was heated to 90 °C under vacuum for one hour to remove any residual  
 solvent.  
 Total yield of liquid, identified as [(C<sub>6</sub>)<sub>3</sub>P(C<sub>14</sub>)]BSB], was 14.51g (18.92mmol,  
 96%).

- 20 - No freezing/melting points observed in the range -150 to 300<sup>0</sup>C.  
 - Solubility: see table 1.  
 - Viscosity: see table 2  
 - Electrochemical stability: see Figure 1  
 - Analysis calculated for C<sub>44</sub>H<sub>76</sub>B<sub>0</sub>P [%]: C, 72.05; H, 9.99; N, 0.00.  
 25 - Found: C; 70.70; H, 10.16; N, 0.05.  
 - <sup>1</sup>H-NMR [300 MHz, δ(TMS in CDCl<sub>3</sub>)] in D<sub>6</sub>-acetone at 25 °C: δ = 7.98 (m, 2  
 H), 7.25 (m, 2 H), 6.73 (m, 4 H) (anion); 2.21-0.75 (m, 68 H, cation)  
 - <sup>13</sup>C-NMR [75.45 MHz, δ(TMS in CDCl<sub>3</sub>)] in CDCl<sub>3</sub> at 25 °C: δ = 165.41,  
 161.21, 135.27, 130.75, 119.42, 117.54 (s, anion); 33.06-14.70 (various s,  
 30 cation)  
 - <sup>31</sup>P-NMR [121.49 MHz] in D<sub>6</sub>-acetone at 25°C: δ = 33.5.

-  $^{11}\text{B}$ -NMR [160.46 MHz,  $\delta(\text{BF}_3 \cdot \text{OEt}_2 \text{ in } \text{D}_2\text{O})$ ] in  $\text{D}_8$ -acetone at 25 °C:  $\delta = 0.20$ .

### Physicochemical characterisation of the salts of the examples

#### 5 Example 4 Determination of solubility

Solubility was determined only qualitatively by mixing approximately 0,5 ml of the ionic liquid with the same amount of organic solvent and shaking. All samples were checked a second time after several hours to ensure, that no

10 slow phase separation had occurred.

Table 1 Solubility of  $[\text{R}_4\text{P}][\text{X}]$  (X = BBB, BSB, BBPB;  $\text{R}_4\text{P}=(\text{C}_6)_3\text{P}(\text{C}_{14})$ )

Solvent	$[\text{R}_4\text{P}][\text{BBB}]$	$[\text{R}_4\text{P}][\text{BSB}]$	$[\text{R}_4\text{P}][\text{BBPB}]$
water	N	N	N
15 acetone	Y	Y	Y
iso-propyl alcohol	Y*	Y	Y*
diethyl ether	Y	Y	Y
tetrahydrofurane	Y	Y	Y
dichloromethane	Y	Y	Y
20 chloroform	Y	Y	Y
hexane	N**	N**	Y
toluene	Y	Y	Y
acetonitrile	Y*	Y*	Y*

25 Y stands for soluble, N stands for not soluble

\* gentle heating required

\*\* mixture becomes cloudy, then separates into two clear layers

Example 5 Determination of viscosity

- Viscosity was measured using an LVDV-II Brookfield Cone and Plate
- 5 Viscometer (1 % accuracy, 0,2 repeatability). The sample cup of the viscometer was fitted with luer and purge fittings, so that a positive current of dry dinitrogen was maintained at all times during the measurements, thus avoiding absorption of atmospheric moisture. The sample cup was jacketed
- 10 6G (+0.1 °C accuracy).

Table 2: Viscosity [cP] of [R<sub>4</sub>P] [X] (X = BBB, BSB, BBPB; R<sub>4</sub>P=(C<sub>6</sub>)<sub>3</sub>P(C<sub>14</sub>))

	Temperature (°C)	[R <sub>4</sub> P]	[R <sub>4</sub> P]	[R <sub>4</sub> P]
		[BSB]	[BBB]	[BBPB]
15	5	7334	-	95020
	10	4241	-	59233
	15	2663	6184	33737
	20	1730	3735	20660
	25	1164	2439	12813
20	30	801.4	1593	8245
	35	566.3	1087	5453
	40	407.0	739.8	3675
	45	300.4	538.1	2703
	50	229.6	386.7	1953
25	55	171.4	288.3	1393
	60	132.6	217.2	1022
	65	106.3	168.2	759.0
	70	85.1	126.3	550.7
	75	68.4	100.2	333.9
30	80	56.4	81.0	209.2
	85	47.2	65.2	173.0

90	39.9	50.2	177.8
95	34.1	40.91	

5 Example 6 Determination of electrochemical stability of [(C<sub>6</sub>)<sub>3</sub>P(C<sub>14</sub>)] [BSB]

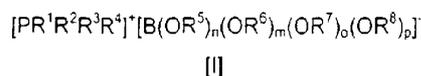
All electrochemical experiments were carried out with an EG&G PARC Model 283 potentiostat/galvanostat connected to a PC through an IEEE-488 bus and controlled using EG&G Parc Model 270/250 Research Electrochemistry  
 10 version 4.23 software. Positive feedback iR compensation was employed to eliminate errors due to solution resistance. The electrochemical cell was constructed from materials purchased from Bioanalytical Systems, Inc. (BAS). The non-aqueous reference electrode was a silver wire immersed in a glass tube containing a 0.100 mol L<sup>-1</sup> solution of AgNO<sub>3</sub> in the [bmim][NO<sub>3</sub>] ionic  
 15 liquid which was separated from the bulk solution by a Vycor plug. All potentials reported are referenced against the Ag(l)/Ag couple. The counter electrode was a platinum coil immersed directly in the bulk solution. For voltammetry, the working disk electrodes used were platinum (A = 2.01 × 10<sup>-2</sup> cm<sup>2</sup>) and glassy carbon (A = 7.07 × 10<sup>-2</sup> cm<sup>2</sup>). The solution was held in a  
 20 glass vial fitted with a Teflon cap with holes for the electrodes and a nitrogen line.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

The claims defining the invention are as follows:

1. Salts of the general formula [I],



wherein

$\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$  denote, in each case independently of one another, a  $\text{C}_{1-20}$  linear, branched or cyclic, saturated or unsaturated aliphatic radical

or a  $\text{C}_{6-20}$ -aromatic or heteroaromatic radical,

wherein the aliphatic, aromatic or heteroaromatic radicals may comprise one or more ether functional groups and/or may be further substituted, preferably further substituted by at least one radical of the formula  $-\text{C}_q\text{F}_{(2q+1-x)}\text{H}_x$ , wherein  $1 \leq q \leq 6$  and  $0 \leq x \leq 2q+1$ ,

$\text{R}^5, \text{R}^6, \text{R}^7$  and  $\text{R}^8$  denote, in each case independently of one another, a  $\text{C}_{6-20}$  aromatic or heteroaromatic radical, that may be further substituted by at least one halogen-radical, preferably a F- or Cl-radical and/or at least one radical of the formula  $-\text{C}_q\text{F}_{(2q+1-x)}\text{H}_x$ , wherein  $1 \leq q \leq 6$  and  $0 \leq x \leq 2q+1$ ,

or a  $\text{C}_{1-8}$ , linear, branched or cyclic, saturated or unsaturated, aliphatic radical, that may be further substituted by at least one halogen-radical, preferably a F- or Cl-radical and/or at least one radical of the formula  $-\text{N}(\text{C}_q\text{F}_{(2q+1-x)}\text{H}_x)_2$ ,  $-\text{O}(\text{C}_q\text{F}_{(2q+1-x)}\text{H}_x)$ ,  $-\text{SO}_2(\text{C}_q\text{F}_{(2q+1-x)}\text{H}_x)$  or  $-\text{C}_q\text{F}_{(2q+1-x)}\text{H}_x$ , wherein  $1 \leq q \leq 6$  and  $0 \leq x \leq 2q+1$ ,

or a carboxylic-, dicarboxylic- or hydroxycarboxylic, linear, branched or cyclic, saturated or unsaturated  $\text{C}_{1-8}$ -aliphatic or  $\text{C}_{6-20}$ -aromatic or

heteroaromatic radical that may be further substituted by at least one halogen-radical, preferably a F- or Cl-radical and/or at least one radical of the formula  $-N(C_qF_{(2q+1-x)}H_x)_2$ ,  $-O(C_qF_{(2q+1-x)}H_x)$ ,  $-SO_2(C_qF_{(2q+1-x)}H_x)$  or  $-C_qF_{(2q+1-x)}H_x$ , wherein  $1 \leq q \leq 6$  and  $0 \leq x \leq 2q+1$ ,

and wherein

at least two of the radicals  $R^1, R^2, R^3, R^4$  may be bound to each other by single or double bonds, and/or

at least two of the radicals  $R^5, R^6, R^7, R^8$  may be bound to each other by single or double bonds,

and  $0 \leq n, m, o, p \leq 4$  and  $m + n + o + p = 4$

and wherein the following salts are disclaimed:

Bis[salicylato(2-)]borate (III)-tetrabutylphosphonium,

Tetrakis[1-naphthalenolato (1-)]-borate-tetraphenylphosphonium,

Bis[2-hydroxybenzoato (2-)]-borate-tetrabutylphosphonium,

Bis[1,2-benzodiolato(2-), O, O']-borate-tetraphenylphosphonium,

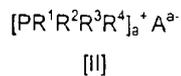
Tetrabutoxy(1-)borate-tetraphenylphosphonium,

Tetrakis(1,1'-biphenyl-4,4'-diolato)-borate-tetraphenylphosphonium,

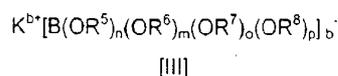
Bis[2,3-naphthalendiolato (2-) O, O']-borate-tetraphenylphosphonium.

2. Salts according to claim 1, wherein at least two of the radicals  $R^1, R^2, R^3, R^4$  are identical and/or bound to each other by single or double bonds.
3. Salts according to claim 1 or 2, wherein at least two of the radicals  $R^5, R^6, R^7, R^8$  are identical and/or bound to each other by single or double bonds.

4. Salts according to any one of claims 1 to 3, wherein at least one of the radicals,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  denotes, in each case independently of one another, a radical selected from the group consisting of phenyl-, naphthyl-, anthracenyl, phenanthrenyl, pyridyl-, pyracyl- or pyrimidyl-radicals, that may be further substituted by at least one halogen radical, preferably a F- or Cl-radical and/or at least one radical of the formula  $-C_qF_{(2q+1-x)}H_x$ , wherein  $1 \leq q \leq 6$  and  $0 \leq x \leq 2q+1$ .
5. Salt according to any one of claims 1 to 4, wherein at least one of the radicals  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  denotes phenyl or  $C_{1-20}$ -alkyl, preferably  $C_6H_{13}$ - oder  $C_{14}H_{29}$ -alkyl.
6. Salt according to any one of claims 1 to 5, wherein at least two of the radicals  $R^5$ ,  $R^6$ ,  $R^7$  or  $R^8$  denote a 2,2'-biphenyl-diolato(2')O,O'-, a 1,2-benzen-diolato(2-)O,O'- or a salicylato(2-)-radical.
7. Salt according to any one of claims 1 to 6, wherein  $[B(OR^5)_n(OR^6)_m(OR^7)_o(OR^8)_p]^-$  denotes bis[2,2'-biphenyl-diolato(2')O,O']-borate, bis[1,2-benzen-diolato(2-)O,O']-borate or bis[salicylato(2-)]-borate.
8. Method for the preparation of salts, wherein a salt of the general formula [II]



and a salt of the general formula [III]



wherein

$A^-$  denotes an anion,  $a= 1$  to  $3$ , preferably  $a=1$ , more preferably an anion chosen from  $Cl$ ,  $Br$  or  $I$ ,

$K^+$  denotes a cation,  $b= 1$  to  $3$ , preferably  $b=1$ , more preferably a cation chosen from  $H$ ,  $Li$ ,  $K$ ,  $Na$ ,  $Ag$  or  $NR_4^+$ ,

and  $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8$ ,  $n, m, o, p$ , have the meanings according to claim 1,

are dissolved in a suitable solvent and mixed and the resulting salt is isolated and/or purified.

9. Method according to claim 8, wherein the resulting salt is purified by separating the byproduct  $K^+A^-$  by precipitation, ionic exchange chromatography or by evaporation, if  $K^+$  denotes hydrogen.
10. Method according to claim 8 or 9, wherein the suitable solvent is acetonitrile or THF (tetrahydrofuran) or a mixture of at least two of these solvents.
11. Method according to claim 8 or 9, wherein the suitable solvent is an aprotic solvent, preferably acetonitrile or THF (tetrahydrofuran) or a mixture of at least two aprotic solvents, wherein the resulting salt  $K^+A^-$  is insoluble.
12. Method according to any one of claims 8 to 11 wherein the mixing of the salts of formula [II] and [III] is performed at a temperature of  $0$  to  $100^\circ C$ , preferably  $0$  to  $50^\circ C$ , more preferably  $10$  to  $40^\circ C$ .

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13. Method according to any one of claim 8 to 12, wherein the reaction is carried out in a solvent or solvent mixture that is directly suitable for use in a secondary or primary battery, a capacitor, a supercapacitor or a galvanic cell.
14. Method according to claim 13, wherein the solvent is an organic carbonate, preferably an ethylenecarbonate, propylenecarbonate, butylene-carbonate, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, methylpropylcarbonate or a mixture of at least two of these solvents.
15. Use of at least one of the salts according to any one of claims 1 to 7 alone or in combination with further salts and/or additives in primary batteries, secondary batteries, capacitors, supercapacitors and/or galvanic cells.
16. Electrolyte, preferably for primary batteries, secondary batteries, capacitors, supercapacitors and/or galvanic cells, comprising at least one compound of the general formula [I] according to any one of claims 1 to 7.
17. Electrolyte according to claim 16, wherein the salt concentration of the electrolyte is 0,01 – 3 mol/l, preferably 0,01 – 2 mol/l, most preferably 0,1 – 1,5 mol/l.
18. Primary battery comprising at least one compound of the general formula [I] according to any one of claims 1 to 7.
19. Secondary battery comprising at least one compound of the general formula [I] according to any one of claims 1 to 7.
20. Capacitor comprising at least one compound of the general formula [I] according to any one of claims 1 to 7.

21. Supercapacitor comprising at least one compound of the general formula [I] according to any one of claims 1 to 7.
22. Galvanic cell comprising at least one compound of the general formula [I] according to any one of claims 1 to 6.
23. Hydraulic liquid comprising at least one compound of the general formula [I] according to any one of claims 1 to 6.
24. Use of a salt according to any one of claims 1 to 7 as an ionic liquid or as a conducting salt in an electrolyte of electrochemical devices.
25. Use of a salt according to any one of claims 1 to 7 as a catalyst, solvent, electrolyte or starting compound for the preparation of organic compounds.
26. Salts of the general formula [I], methods for their preparation, electrolytes batteries, capacitors and galvanic cells containing same and/or uses thereof substantially as herein described with reference to the Examples.

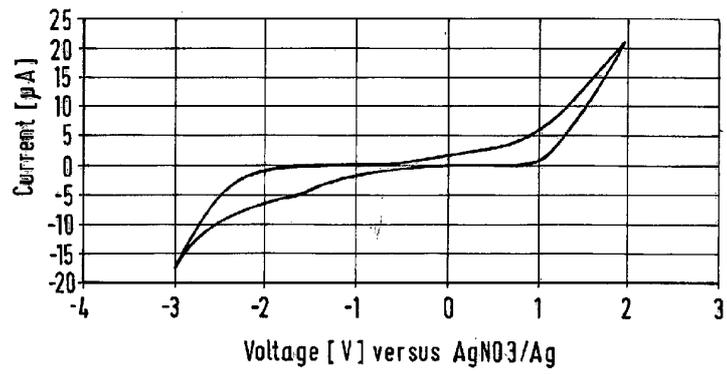


Fig. 1

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