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Electrochemical and spectroscopic characterisation of barium acid salts of 3,5-disulfophenylphosphonic acid

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Barium salts of 3,5-disulfophenylphosphonic acid (H_4Y) having formulae Ba_2Y, $Ba_{1.8}H_{0.4}Y$, BaKHY and BaH_2Y have been prepared and characterised by X-ray powder diffraction, thermogravimetry, IR spectroscopy, ac conductivity and e.m.f. measurements. Ba_2Y is orthorhombic, with $a=8.126$, $b=4.691$, $c=8.649$ Å; $Ba_{1.8}H_{0.4}Y$ and BaKHY have similar cell parameters to these. BaH_2Y is also orthorhombic, but with all cell parameters close to double those of the former salts. The anhydrous salts are stable in air up to at least 300 °C. The ac conductivity (σ) has been measured at 100 °C and controlled relative humidity (RH) in the range 50–80%; at 70% RH, σ increases from *ca.* 10^{-8} up to *ca.* 10^{-2} S cm^{-1} according to the sequence: $Ba_2Y < Ba_{1.8}H_{0.4}Y < BaKHY < BaH_2Y$. Electromotive force measurements have shown K^+ and H^+ to be the main charge carriers in BaKHY and BaH_2Y, respectively. In both salts protons are localized on the phosphonate group at 53% RH, but IR spectroscopy provides evidence for a degree of proton transfer to water molecules in BaH_2Y at 75% RH.

Phosphonic acids, RPO_3H_2 (R = alkyl or aryl group), and metal ions (M^{n+}, $n=2, 3, 4$) yield a large number of salts with layered structures,[1] where the spacing between metal layers depends on the length of the pendant RPO_3^{2-} anion. The interest in this kind of material is motivated by the fact that their physical properties can be modulated to a great extent by a suitable choice of the group attached to the phosphorus atom. The salts of sulfoalkyl- or sulfoaryl-phosphonic acids have not been much studied, probably because the free acids themselves are little known. Yet these salts are of considerable potential interest since the presence of sulfonic acid groups is expected to affect significantly their performance in acid catalysis, ion exchange and ion conductivity.[2] Recent investigations showed that α- and γ-layered metal(IV) sulfoarylphosphonates exhibit high proton conductivities, of the order of 0.01 S cm^{-1}, as the relative humidity approaches 100%.[3–6]

It was therefore of interest to undertake an investigation of the acid salts of sulfophenylphosphonic acids with metal(II) ions. The present work reports the preparation of barium–potassium acid salts of 3,5-disulfophenylphosphonic acid of formula Ba_2Y, $Ba_{1.8}H_{0.4}Y$, BaKHY and BaH_2Y, $Y = [C_6H_3PO_3(SO_3)_2]^{4-}$, and their characterisation by X-ray powder diffractometry, IR spectroscopy, ac conductivity and e.m.f. measurements.

Experimental

3,5-Disulfophenylphosphonic acid [$C_6H_3PO_3H_2(SO_3H)_2$, hereafter H_4Y] was prepared by reacting phenylphosphonic acid with sulfur trioxide at 200 °C, as reported in ref. 7. Barium salts of 3,5-disulfophenylphosphonic acid were synthesised by mixing, in stoichiometric amounts, a water solution of H_4Y with barium and potassium hydroxide solutions and subsequently evaporating the solvent to dryness at 80 °C. The formulae of the barium salts were calculated from the initial reagent ratios and found to be consistent with the results of the analytical determinations of acidic hydrogens, barium and carbon. All analyses were carried out on products dried to constant mass at 180 °C. Barium was determined as $BaSO_4$, after dissolving the solids in water and diluted HCl. The amount of acidic hydrogen was determined by titration with 0.1 M NaOH to phenolphthalein end point in water. For insoluble products, the samples were put in a closed vessel blanketed with argon and digested for 48 h at room temperature in a known excess of NaOH; the alkali excess was then titrated with 0.1 M HCl. Carbon was determined by a Carlo Erba model 1106 microanalyser.

Found (f) and theoretical (th) data for barium (mass%): 46.5 (f) and 46.6 (th) for Ba_2Y, 44.2 (f) and 44.0 (th) for $Ba_{1.8}H_{0.4}Y$, 27.9 (f and th) for BaKHY, 30.1 (f) and 30.3 (th) for BaH_2Y. Found and theoretical data for acidic hydrogen (H^+, mequiv. g^{-1}): 0.713 (f) and 0712 (th) for $Ba_{1.8}H_{0.4}Y$, 2.00 (f) and 2.03 (th) for BaKHY, 4.45 (f) and 4.41 (th) for BaH_2Y. Found and theoretical data for carbon (mass%): 12.3 (f) and 12.2 (th) for Ba_2Y, 13.0 (f) and 12.8 (th) for $Ba_{1.8}H_{0.4}Y$, 14.9 (f) and 14.7 (th) for BaKHY, 15.7 (f) and 15.9 (th) for BaH_2Y.

Thermogravimetric determinations were carried out in air using a Stanton Redcroft thermal analyser STA 780 at a heating rate of 5 °C min^{-1}. IR spectra were collected with a Bruker IFS 113V Fourier spectrometer on samples pressed into pellets with KBr. XRD powder patterns were recorded on a computer controlled Philips PW 1710 diffractometer using Cu-Kα radiation (40 kV, 30 mA). Data were collected by a step scanning procedure at $4 \leqslant 2\theta \leqslant 60°$, with a step size of 0.02° and a count time of 10 s per step. The patterns were mathematically stripped of the $K\alpha_2$ contribution and then indexed with the TREOR program.[8] Densities ($D_m \pm 0.05$ g cm^{-3}) were picnometrically determined in CCl_4. ^1H and ^{31}P liquid state NMR spectra were taken with a Bruker AC200 instrument on solutions prepared by dissolving 50 mg of solid in *ca.* 0.5 ml of 0.3 M DCl in D_2O.

Ac conductivity measurements were carried out on pressed powders according to the impedance technique by means of an HP 4192A impedance analyser (frequency range 10 Hz to 10 MHz, signal level $\leqslant 100$ mV). Pellets, 10 mm in diameter and 1–1.5 mm thick, were prepared by pressing *ca.* 200 mg of material at 50 kN cm^{-2}. The two flat surfaces of the pellet were coated with a composite electrode consisting of a mixture of platinum black (Ventron) with the disulfophenylphosphonate material in the ratio 3:1. Measurements at 100 °C and controlled relative humidity were carried out using a sealed cell consisting of two adjacent cylindrical compartments connected by a hole and held at different temperatures; the cold compartment contained water, while the hot compartment housed the pellet under test.

Electromotive force measurements were carried out at 80 °C and 63% relative humidity on a two pellet system consisting of a barium salt pellet in contact with a $Zr(O_3POH)_2{\cdot}H_2O$ pellet; the free flat surfaces of the pellets were coated with pressed Pt-black (Ventron) and connected to an HP44701A voltmeter. Before starting the measurements the cell was purged with humidified nitrogen for one day. During the measurements the cell was flushed with a humidified nitrogen–hydrogen mixture (4% H_2). The relative humidity was controlled by bubbling the purging gas in water heated at 69 °C. The tube connecting the humidifier to the cell was kept at a temperature higher than that of the humidifier to avoid vapour condensation.

Results and Discussion

Fig. 1 shows the mass loss curves of $BaKHY{\cdot}0.5H_2O$ and $BaH_2Y{\cdot}2H_2O$. In both cases there are two well defined steps: the first step up to 150–200 °C and the second between 350 and 650 °C. Since the decomposition of the sulfonic groups in zirconium sulfophenylphosphonates starts above 200 °C,[4] the first step can reasonably be attributed to the loss of water. To prove this, samples which had been conditioned at 53% relative humidity were heated at 180 °C up to constant mass and again stored at 53% relative humidity: all samples recovered 90% of the mass loss, at least. To check the integrity of the organic anion after the thermal treatment, NMR spectra were collected for solutions obtained by dissolving $Ba_{1.8}H_{0.4}Y$ and BaH_2Y in D_2O–DCl: heated and non-heated samples showed the same ^1H and ^{31}P spectra. The disulfophenylphosphonate anion is therefore stable up to at least 180 °C and the water content of the barium salts can be calculated from the first step of the mass loss curve. The water content of the compounds listed in Tables 1 and 2 refers to samples which had previously been conditioned at 53% relative humidity.

The XRD patterns (Table 1) were indexed in the orthorhombic system; cell parameters are reported in Table 2. $Ba_2Y{\cdot}H_2O$, $Ba_{1.8}H_{0.4}Y{\cdot}1.2H_2O$ and $BaKHY{\cdot}0.5H_2O$ have similar cell axes and each cell contains one formula unit. It is therefore concluded that the potassium hydrogen form is obtained by isomorphous substitution of K^+ for Ba^{2+} in the barium form.

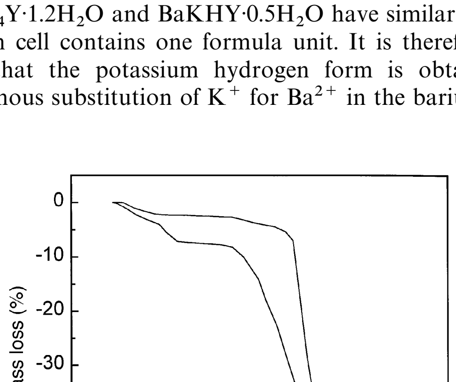

Fig. 1 Mass loss curves of $BaKHY{\cdot}0.5H_2O$ and $BaH_2Y{\cdot}2H_2O$; heating rate 5 °C min^{-1} [$Y=C_6H_3PO_3(SO_3)_2{}^{4-}$]

The cell parameters of these compounds correspond approximately to the dimensions of the 3,5-disulfophenylphosphonate anion.[3] $BaH_2Y{\cdot}2H_2O$ is also orthorhombic but the unit cell contains eight formula units and each axis is close to double that of the corresponding axis of $Ba_2Y{\cdot}H_2O$.

A preliminary electrochemical characterisation of the compounds, listed in Table 1, was carried out by ac conductivity measurements at 100 °C as a function of relative humidity (RH). At 70% RH, the conductivity of Ba_2Y is $<10^{-8}$ S cm^{-1} (Fig. 2); however partial replacement of H^+ and K^+ for Ba^{2+} results in a strong enhancement of the conductivity, giving values up to 10^{-2} S cm^{-1}, according to the sequence: $Ba_2Y < Ba_{1.8}H_{0.4}Y < BaKHY < BaH_2Y$. The highest conductivity, $\sigma = 0.12$ S cm^{-1}, was measured for BaH_2Y at 80% RH. Taking into account that Ba_2Y and $Ba_{1.8}H_{0.4}Y$ are poor conductors, the high conductivity of the isomorphous BaKHY has to be ascribed to the increase of the concentration of the monovalent cations. Further conductivity measurements were carried out at 20 °C on BaH_2Y. With increasing relative humidity from 53 to 75%, σ rises from 2×10^{-4} to 3×10^{-3} S cm^{-1} and the water content from two to three molecules per unit formula.

The dependence of conductivity on the degree of hydration of the most conductive materials was also investigated at 100 °C. Fig. 3 shows the water content, at 100 °C, as a function of relative humidity. From Fig. 2 and 3 it is seen that on increase of the relative humidity from 45 to 60%, the conductivity of BaKHY increases by an order of magnitude while the bulk water content remains constant. Consequently, within this relative humidity range at least, bulk transport is negligible and the conduction is dominated by transport through grain boundaries and/or on the free surface of the particles. On the other hand, the fact that the conductivity of BaH_2Y increases with increasing bulk hydration and is higher than that of BaKHY by at least an order of magnitude suggests that BaH_2Y is mainly a bulk conductor.

The nature of the cationic charge carriers was investigated using the following electrochemical cell:

$$H_2(p_1,RH_1),\ Pt|Ba_{(4-k-h)/2}K_kH_hY|\alpha\text{-}Zr(HPO_4)_2{\cdot}H_2O\ |Pt,\ H_2(p_2,\ RH_2) \qquad (1)$$

where the ionic conductor under test ($Ba_{(4-k-h)/2}K_kH_hY$) is in contact with a proton conductor [α-$Zr(HPO_4)_2{\cdot}H_2O$]. Electromotive force measurements were carried at $T=80$ °C with $p_1=p_2=0.04$ atm and $RH_1=RH_2=63\%$. Under these conditions, according to ref. 9, the e.m.f. of the cell is zero only if $Ba_{(4-k-h)/2}K_kH_hY$ is a pure proton conductor. However, if the transport number of one of the metal ions is not negligible in comparison with that of the proton, an e.m.f. will appear across the cell with the positive pole on the side of α-$Zr(HPO_4)_2{\cdot}H_2O$, due to the diffusion of the mobile cation into the proton conductor. The results of these measurements are listed in Table 3. For $Ba_{(4-k-h)/2}K_kH_hY = BaKHY$ the e.m.f. is largely positive, indicating that BaKHY is a surface metal ion conductor. Under the assumption that K^+ is much more mobile than Ba^{2+}, the proton transport number in BaKHY can be roughly estimated to be no higher than 0.01 by using the equation $\phi_2-\phi_1=-(RT/F)\ \ln\ t(H)$, where $t(H)$ is the proton transport number in the mixed conductor.[10] For $Ba_{(4-k-h)/2}K_kH_hY = BaH_2Y$ and $Ba_{(4-k-h)/2}K_kH_hY = Ba_{1.8}H_{0.4}Y$ the e.m.f. is zero within the error limits. On the other hand, if $Ba_{(4-k-h)/2}K_kH_hY$ is replaced by a pellet of $BaCl_2{\cdot}H_2O$, the e.m.f. of the cell is +107 mV showing that when a barium electrolyte containing no mobile protons is coupled with α-zirconium phosphate, then the e.m.f. of the cell is significantly different from zero, with the positive pole at the expected side. Therefore, BaH_2Y and $Ba_{1.8}H_{0.4}$ are both proton conductors.

Information on the nature of the protonic species present in

Table 1 X-Ray powder patterns of barium salts of 3,5-disulfophenylphosphonic acid [$Y=C_6H_3PO_3(SO_3)_2^{4-}$]

$Ba_2Y{\cdot}H_2O$		$Ba_{1.8}H_{1.8}Y{\cdot}1.2H_2O$		$BaKHY{\cdot}0.5H_2O$		$BaH_2Y{\cdot}2H_2O$	
d/Å	$100I/I_0$	d/Å	$100I/I_0$	d/Å	$100I/I_0$	d/Å	$100I/I_0$
8.064	60	8.127	84	8.194	45	15.147	5
4.666	98	4.698	100	4.728	45	9.087	18
4.107	65	4.118	58	4.116	100	8.370	20
4.052	28	4.066	32	3.729	58	5.892	18
3.792	55	3.801	41	3.136	68	5.091	25
3.162	95	3.171	62	3.096	12	4.946	55
3.061	30	3.073	23	2.929	13	4.713	30
2.946	20	2.954	14	2.904	8	4.182	25
2.883	8	2.892	8	2.731	50	3.906	97
2.700	100	2.709	70	2.490	17	3.779	20
2.493	35	2.499	19	2.406	4	3.627	48
2.338	10	2.346	6	2.288	15	3.595	60
2.286	40	2.292	20	2.272	14	3.493	80
2.247	35	2.254	20	2.096	10	3.446	100
2.147	18	2.059	30	2.060	27	3.382	30
2.054	60	2.033	8	1.998	4	3.336	15
2.026	12	1.995	8	1.916	7	3.038	99
1.990	15	1.952	7	1.880	3	2.950	45
1.953	18	1.865	7	1.866	2	2.789	90
1.859	8	1.774	8	1.841	2	2.684	20
1.768	20	1.737	4	1.788	3	2.522	25
1.732	7	1.682	5	1.749	4	2.375	18
1.634	25	1.638	10	1.736	2	2.280	28
		1.563	5	1.663	5	2.246	25
				1.645	7	2.110	35
				1.578	3	2.067	20
						2.041	27
						2.004	35

Table 2 Cell parameters of barium salts of 3,5-disulfophenylphosphonic acid [$Y=C_6H_3PO_3(SO_3)_2^{4-}$]

compound	$Ba_2Y{\cdot}H_2O$	$Ba_{1.8}H_{0.4}Y{\cdot}1.2H_2O$	$BaKHY{\cdot}0.5H_2O$	$BaH_2Y{\cdot}2H_2O$
a/Å	8.104	8.129	8.187	15.127
b/Å	4.677	4.691	4.732	9.428
c/Å	8.582	8.596	8.385	18.139
V/Å^3	325.2	327.8	324.8	2587
M(20)[a]	55	57	43	17[b]
Z	1	1	1	8
D_c/g cm^{-3}	3.10	2.95	2.56	2.53
D_m/g cm^{-3}	2.92			2.45

[a] M(20) is a figure of merit referred to the first 20 reflections of the pattern according to ref. 8. [b] The value is referred to M(18).

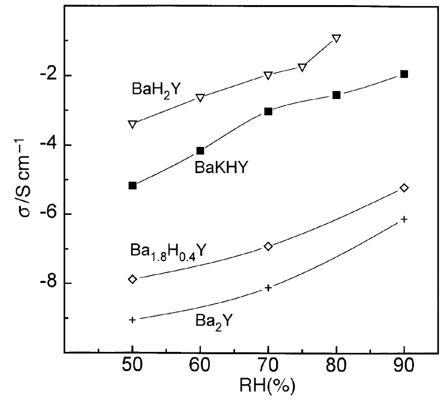

Fig. 2 Ac conductivity, at 100 °C, of barium salts of 3,5-disulfophenylphosphonic acid [$Y=C_6H_3PO_3(SO_3)_2^{4-}$] as a function of relative humidity

the various salts was derived from IR spectroscopy. Questions that arise concern the localisation of the proton(s) in $BaKHY{\cdot}0.5H_2O$ and $BaH_2Y{\cdot}2H_2O$ on one or other of the conjugate base sites (sulfonate, phosphonate) of the aromatic ring and/or their association with water of crystallisation to form proton hydrates, H_3O^+ for example. Ba_2Y and BaK_2Y, free of acidic hydrogen, are expected to give IR spectra that

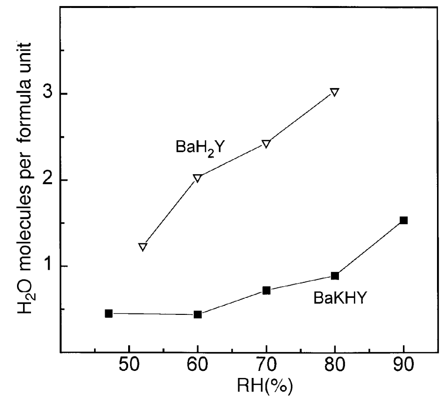

Fig. 3 Water content, at 100 °C, of BaKHY and BaH_2Y [$Y=C_6H_3PO_3(SO_3)_2^{4-}$] as a function of relative humidity

Table 3 E.m.f. values for cell (1) at 80 °C and 63% RH [$Y=C_6H_3PO_3(SO_3)_2^{4-}$]

compound	$(\phi_2-\phi_1)$/mV
BaH_2Y	−1
$Ba_{1.8}H_{0.4}Y$	0
BaKHY	+159

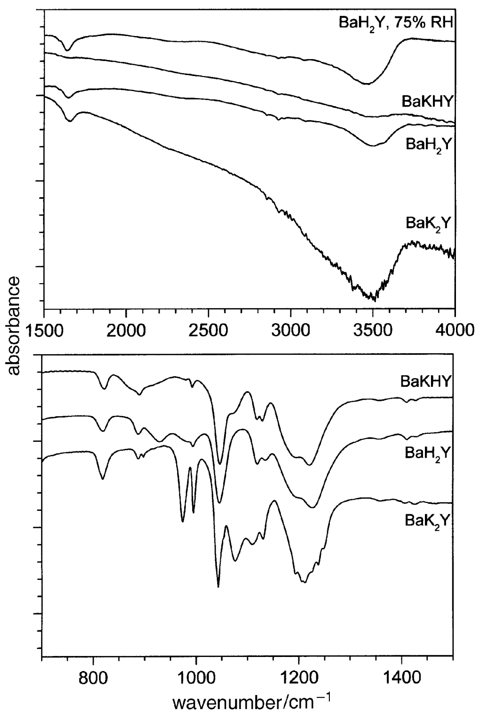

Fig. 4 IR spectra of BaK_2Y, BaKHY and BaH_2Y [$Y = C_6H_3PO_3(SO_3)_2^{4-}$] for samples equilibrated at 53% relative humidity; the mid–high frequency region of the spectrum of BaH_2Y equilibrated at 75% RH is also shown

show the presence only of sulfonate and phosphonate groups and water molecules (in addition to absorption arising from the phenyl ring). The assignment of the phosphonate/sulfonate bands was based on ref. 11. In the 960–1250 cm^{-1} region, these two compounds have virtually identical spectra, with bands at 1215 (shoulder at 1193) and 1043 cm^{-1} given by symmetric and antisymmetric stretching vibrations $\nu_{as}(SO_3^-)$ and $\nu_s(SO_3^-)$ respectively, and weaker absorption at 1109, 1076 and 974 cm^{-1} identified as $\nu_{as}(PO_3^{2-})$ and $\nu_s(PO_3^{2-})$. As an example Fig. 4 shows the spectrum of BaK_2Y.

In the spectra of the acid salts $BaKHY{\cdot}0.5H_2O$ and $BaH_2Y{\cdot}2H_2O$, the former group of bands attributed to the sulfonate group remains unchanged in position and relative intensity, suggesting that these sites remain unprotonated. $BaKHY{\cdot}0.5H_2O$ gives a pattern at 1220 (shoulder at 1193) and 1046 cm^{-1}, for example. In contrast, modifications can be observed in number and intensity of bands assigned to the phosphonate group, and a new absorption is seen at a position characteristic of the stretching vibration of protonated $-P-OH$. Thus for $BaKHY{\cdot}0.5H_2O$ bands at 1119 (weak) and a shoulder at 1080 cm^{-1} result from $\nu_{as}(PO_2^-)$ and $\nu_s(PO_2^-)$, and that at 900 cm^{-1} from $\nu(POH)$. Further changes are seen in $BaH_2Y{\cdot}2H_2O$, where the shoulder given by $\nu_{as}(PO_2^-)$ has disappeared, absorption at 1119 cm^{-1} is attributed to $\nu(PO)$ and the bands at 970 and 929 cm^{-1} to $\nu_{as}[P(OH)_2]$ and $\nu_s[P(OH)_2]$, respectively.

All of the salts show similar patterns in the high and mid frequency region: broad $\nu(OH)$ of water of maximum at *ca.* 3450–3500 cm^{-1}, and the corresponding $\delta(H_2O)$ at 1635–1650 cm^{-1}. The former is too high and the latter too low to suggest the existence in any of the systems of oxonium ions. Finally, the spectra also indicate that hydrogen bonding in the salts is weak, since in no case does the breadth of the absorption in the high frequency region extend below *ca.* 3200 cm^{-1}.

The absorption pattern of BaH_2Y in the region 1500–3800 cm^{-1} is significantly altered both in intensity and position following equilibration of the sample at 75% RH. Most strikingly, in the higher frequency region, a broad band extends from *ca.* 3600 to *ca.* 2000 cm^{-1} with maxima at 3500, 2880 and 2300 cm^{-1}. Whilst certainly indicative of the presence of hydrogen bonding of medium strength, the maximum at 2880 cm^{-1} may also be the signature of the ν_1/ν_3 modes of the H_3O^+ ion. Typical spectra of simple oxonium salts such as H_3ONO_3,[12] H_3OCl[13] or H_3OClO_4[14] or even the more complex $H_3O^+CH_3C_6H_4SO_3^-$,[15] and $(H_3O)M^{III}(SO_4)_2$[16] absorb in three regions: a broad envelope between 3380 and 2460 cm^{-1}, (ν_1/ν_3); 1720–1650 cm^{-1} (ν_4); 1140–950 cm^{-1} (ν_2). In the case of BaH_2Y, the band at 1630 cm^{-1} due to the scissoring mode of water has also widened, and a distinct shoulder is observed at *ca.* 1780 cm^{-1}, but the lowest of these regions is occupied by vibrations of the disulfophenylphosphonate group and is of little diagnostic use. The formation of hydrogen bonding on increasing hydration in the RH range from 53 to 75% can itself account for the high proton conductivity of BaH_2Y at high relative humidity.

Conclusion

Barium acid salts of 3,5-disulfophenylphosphonic acid ($Ba_{0.8}H_{0.4}Y$, BaH_2Y) were demonstrated to be proton conductors. In comparison with zirconium sulfoarylphosphonates,[4,5] the conductivity of BaH_2Y appears to be dependent on relative humidity to a greater extent. In particular, at 100 °C and 50% RH, BaH_2Y is less conductive than γ-zirconium sulfophenylphosphonate by a factor of five, being however more conductive by about the same factor at 80% RH. At this relative humidity the conductivity of BaH_2Y is the highest among those measured to date for sulfoarylphosphonates. Finally it was shown that, unlike layered zirconium sulfoarylphosphonates of the α- and γ-type,[3–6] where the acidic protons belong to the sulfonate group, in the barium salts protons are localised on the phosphonate group.

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