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High-Yield Synthesis and Crystal Structure Determination of Sodium Triphenylphosphane Monosulfonate (TPPMS^{Na})

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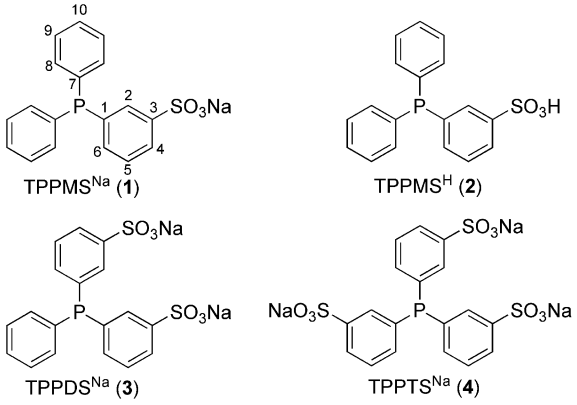
A simple, high-yield synthesis is described that leads to the sodium salt of monosulfonated triphenylphosphane (TPPMS^{Na}) as a pure product in large quantities without complicated workup techniques. The single-crystal X-ray structure of TPPMS^{Na}·2.5H_2O is reported. The structure is built up by alternating layers of aquated sodium sulfonate units and hydrophobic triphenyl units. Thermogravimetric analyses show the loss of one molecule of water at 70 and one at 105 °C. Thermal decomposition occurs at temperatures above 400 °C. The anhydrous ligand is hygroscopic. The preparation of the free acid TPPMS^{H} starting from the sodium salt is also reported. TPPMS^{H} is an extremely hygroscopic solid that could not be isolated in the crystalline form.

Introduction

The synthesis of sodium triphenylphosphane monosulfonate (**1**), abbreviated in the following as TPPMS^{Na} (Scheme 1), was first described by Chatt et al. in 1958.[1] They added triphenylphosphane slowly with cooling to oleum (H_2SO_4/SO_3), then heated the mixture, neutralized carefully with sodium hydroxide after 1–2 h and isolated the product after recrystallization from ethanol in a yield of 32%. Since this first appearance of TPPMS^{Na} in the literature, many similar preparation methods have been proposed.[2–5] Slow addition of triphenylphosphane and heating of the reaction mixture as described by Chatt were not questioned over the years. Purification steps like extraction of the sulfonated product with triisooctylamine in toluene or the intermediate isolation of the ammonium salt of TPPMS have been introduced to isolate TPPMS^{Na} free of impurities.

In this paper, we describe a simple procedure that leads to TPPMS^{Na} as a pure product in large quantities without implementing complicated workup techniques. We determined the single-crystal X-ray structure of the sodium salt and we further characterized this compound by thermogravimetry and ^{31}P NMR spectroscopy. In addition, we describe an easy way to obtain the free sulfonic acid TPPMS^{H} (**2**).



Scheme 1. Sulfonated triphenylphosphanes.

Results and Discussion

To synthesize TPPMS^{Na} effectively, the reactions to avoid are oxidation of the phosphane and the formation of the di- and trisulfonated phosphane. We have found that very slow addition of triphenylphosphane to the cooled oleum solution, as it is described in most references, results in higher amounts of disulfonated triphenylphosphane. Best results were obtained when the triphenylphosphane was added in one portion to the oleum cooled to 0 °C with very effective stirring until all of the phosphane has dissolved. The often mentioned heating of the reaction mixture after dissolution of triphenylphosphane is counterproductive, as it increases the relative amounts of the phosphane oxide. In our hands, the reaction time shortens to a few hours but the oxidation ratio reaches up to 30%. Running the reaction at or below room temperature suppresses the oxidation of the phosphane ligand almost completely.[6] The reaction

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mixture obtained after rapid addition of triphenylphosphane and no heating contains after 18 h mono- and disulfonated triphenylphosphane and small amounts (<5%) of the oxides (Table 1).

Table 1. Composition of the reaction mixture after 18 h quantified by integration of the $^{31}P\{^1H\}$ NMR signals.

TPPMS (**1**)	TPPDS (**2**)	OTPPMS[a]	OTPPDS[a]
75%	22%	2%	1%

[a] Phosphane oxides of **1** and **2**.

Further important changes were made in the workup procedure. It was proposed not to neutralize the reaction mixture completely, but to raise the pH value only to 2–3 to suppress oxidation. It is assumed that the acidic medium protects the phosphane by protonation. Our experiments show that complete neutralization does not increase the amount of oxidized product. However, very effective cooling conditions during neutralization are important so that local overheating of the reaction mixture is minimized. When we tried to separate TPPMS^{Na} from the neutralized reaction mixture we found out that TPPMS^{Na} is practically insoluble in a saturated solution of sodium sulfate. An important step was therefore to estimate the amount of additional water during neutralization so that the final mixture becomes a saturated solution of sodium sulfate. Sodium sulfate is therefore more than a byproduct; it is the adjuvant for separation, when used appropriately. After filtration, the product was recrystallized from water to get rid of small amounts of sodium sulfate. The solubility of both sodium sulfate and TPPMS^{Na} are strongly temperature dependent. From the data in Table 2 it is clear that the recrystallization should be done at 0 °C. After drying, the ligand is stirred in *n*-pentane to wash out unreacted triphenylphosphane. This procedure has to be done thoroughly, because TPPMS^{Na} is known to be a surface-active agent[3] and probably helps to keep triphenylphosphane in solution. To support this separation an ultrasonic bath can be used.

Table 2. Solubility of Na_2SO_4 and TPPMS^{Na} in water.

Temperature [°C]	Solubility TPPMS^{Na}·2H_2O [mmol g^{-1}]	Solubility Na_2SO_4 [mmol g^{-1}][a]
0	1.5	32
22	10	–
25	–	154
40	52	229

[a] Data taken from ref.[7]

TPPMS^{Na} crystallizes with 2.5 molecules of water (see crystal structure determination). Thermogravimetric analyses show a weight loss of 4.1 and 4.9% corresponding to the loss of ca. one molecule of water each at 70 and one at 105 °C. Thermal decomposition occurs at temperatures above 400 °C. The ligand dried in vacuo is hygroscopic and reabsorbs water over a period of several hours.

TPPMS^{H}

When an aqueous solution of TPPMS^{Na} is treated with concentrated hydrochloric acid, a dense white precipitate forms. After about 30 min separation into two clear, colourless liquid phases is observed. The viscous lower phase contains the free acid TPPMS^{H} that can be isolated as a noncrystalline and extremely hygroscopic off-white solid by evaporation of the solvent. Shaking the two-phase system leads again to a white emulsion. Addition of more concentrated hydrochloric acid to the milky emulsion yields a homogeneous solution. The reason for this behaviour is not yet clear. One can assume that the first protonation occurs at the phosphorus atom to form a phosphonium sulfonate, that is, a betaine-type structure. The formation of the white precipitate is not restricted to hydrochloric acid. It is observed also upon addition of sulfuric acid or nitric acid to an aqueous solution of TPPMS^{Na}.

Crystal Structure of TPPMS^{Na}

The sodium salt of TPPMS crystallized in the triclinic space group $P\bar{1}$ with 4 TPPMS^{Na} and 10 water molecules in the asymmetric unit. As a representative example, one TPPMS^{Na} molecule is shown in Figure 1. The structure is built up by alternating layers of aquated sodium sulfonate units and the hydrophobic triphenyl units (Figure 2). These layers are oriented perpendicular to the *c* axis of the cell. The sodium cations are all octahedrally coordinated by six oxygen atoms with Na–O distances varying between 2.25 and 2.61 Å. Na1 and Na21 are coordinated by three sulfonate and three water oxygen atoms, whereas Na41 and Na61 are coordinated by one sulfonate and five water oxygen atoms (Figure 3).

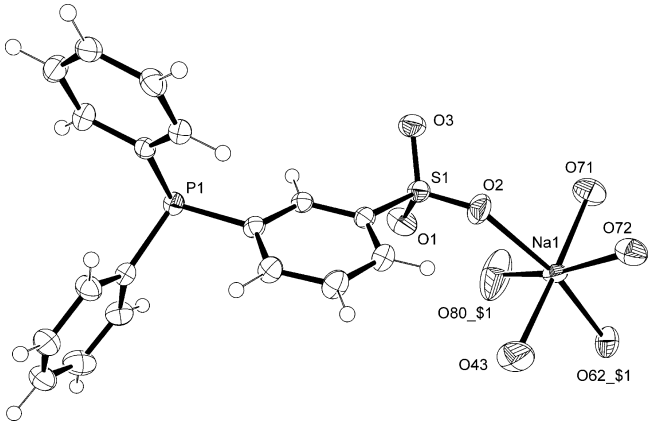

Figure 1. ORTEP presentation of one out of four crystallographic independent TPPMS^{Na} molecules including all five other oxygen atoms that are coordinated to Na1. Ellipsoids are drawn at 50% probability level. Used symmetry operator: \$1: –*x* – 1, –*y* – 2, –*z* + 1. O43 and O62_\$1 are oxygen atoms of other sulfonate groups whereas O71, O72 and O80_\$1 are oxygen atoms of water molecules. Hydrogen atoms of water molecules and one disordered water molecule were omitted for clarity.

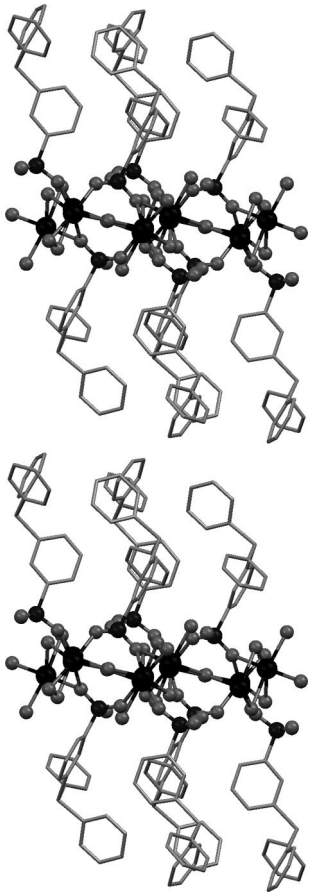

Figure 2. Packing diagram of sodium triphenylphosphane monosulfonate. Only the major components of the disordered water molecules are shown.

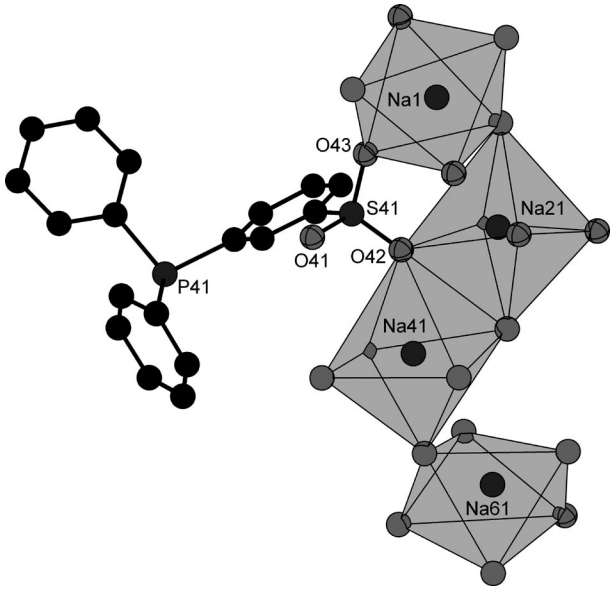

Figure 3. Diagram of one of the four $TPPMS^{Na}$ molecules and the four crystallographically independent oxygen coordinated sodium atoms. The hydrogen atoms and the minor components of the disordered water molecules are omitted for clarity. The NaO_6 octahedra are connected through shared vertices and edges. Oxygen atoms that belong to sulfonate groups of TPPMS are marked with front ellipses.

Characteristics in NMR Spectroscopy

$TPPMS^{Na}$, $TPPDS^{Na}$ and $TPPTS^{Na}$ give rise to signals at –5.9, –5.5 and –5.1 ppm, respectively, in the $^{31}P\{^1H\}$ NMR spectrum in H_2O at pH 5 or above. The introduction of each sulfonate group shifts the signal downfield by 0.4 ppm. A similar shift of 0.6 ppm per sulfonate group was reported by Atwood et al. for the spectra of triphenylphosphane, $TPPMS^{Na}$, $TPPDS^{Na}$ and $TPPTS^{Na}$ in $[D_6]$-DMSO.[8] Below pH 5, the chemical shifts of the ^{31}P NMR signals of the sulfonated phosphanes become pH dependent (Figure 4). The downfield shift of the signal of the monosulfonated triphenylphosphane TPPMS is most pronounced. In 5 M hydrochloric acid the TPPMS chemical shift is 5 ppm, which is 11 ppm lower than that at pH 7. The signal of the trisulfonated phosphane moves only by 6.3 ppm. The $^{31}P\{^1H\}$ NMR signals of the oxidized forms of the sulfonated phosphanes appear at +37.3 (OTPPMS), +36.3 (OTPPDS) and +35.2 ppm (OTPPTS) at neutral pH. In 5 M HCl they are shifted to 38.6, 37.1 and 35.7 ppm, respectively. Again, the signal of the monosulfonated species shows the strongest downfield shift. It is reasonable to assume that this reflects the influence of the electron-withdrawing sulfonate groups on the degree of protonation of the phosphorus in the phosphanes and the oxygen in the phosphane oxides. The proton coupled ^{31}P NMR spectrum of TPPMS in 5 M and even in concentrated HCl does not show $^1J_{P,H}$ coupling. The lifetime of the protonated phosphane is obviously too short. However, in ca. 10 M sulfuric acid and in nonaqueous acids like trifluoracetic acid the coupling constant $^1J_{P,H}$ = 510 Hz is observed, which confirms protonation at phosphorus.

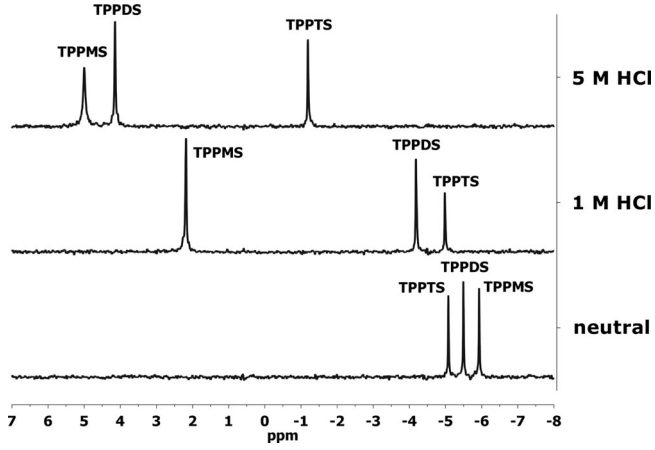

Figure 4. Downfield shift and peak intensities of sulfonated phosphanes in the $^{31}P\{^1H\}$ NMR spectra at different pH values.

The second effect when lowering the pH value is that with increasing downfield shift the signals appear with increasing intensity. The reason for this artefact is the relaxation time of the phosphorus nuclei in the phosphanes and its dependence on the degree of protonation. We measured the relaxation time T_1 in neutral aqueous solution by using inversion recovery with power gated decoupling (Table 3). It was surprising for us to see that the phosphorus relax-

ation times of the three sulfonated phosphanes are not only rather long but also quite different. In addition, protonation shortens the relaxation times significantly. These two effects lead to inaccurate and pH-dependent signal intensities under standard measuring conditions (2 s delay time, 30° pulses).

Table 3. Relaxation times T_1 [s] of the phosphorus nuclei in the sulfonated phosphanes and the corresponding oxides in aqueous solution.

	TPPMS^{Na}	TPPDS^{Na}	TPPTS^{Na}
Water (pH ≈ 7)	5.3	10.3	8.9
1 M HCl (pH ≈ 0)	2.1	5.7	9.2
	OTPPMS^{Na}	OTPPDS^{Na}	OTPPTS^{Na}
Water (pH ≈ 7)	8.9	7.3	5.9

Conclusions

We have presented here a simple, fast and high-yield preparative method for the monosulfonated triphenylphosphane TPPMS^{Na}. Our procedure gives analytically pure TPPMS^{Na} with a yield (59%) twice as high as that reported in *Inorganic Syntheses* (29%).[5] There are discrepancies in the literature about the water content of TPPMS^{Na}. We characterized this sodium salt by thermogravimetric measurements and determined its crystal structure with the composition TPPMS^{Na}·2.5H_2O. The easy access of TPPMS^{Na} can be the basis for further studies of this molecule that can act as an anionic surfactant and as a phosphane ligand at the same time. This property might be especially helpful in the development of metal complexes in biphasic catalysis.[9–11]

Experimental Section

General: TPPDS[12] and TPPTS,[13] used as reference materials, were synthesized according to literature methods. NMR spectra were recorded with a Bruker Avance DRX 200 and a Bruker Avance DRX 500 spectrometer. $^{31}P\{^1H\}$ NMR chemical shifts were referenced to external phosphoric acid (85%) with downfield values taken as positive. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts were referenced to 3-(trimethylsilyl)propanesulfonic acid sodium salt. DEPT-135 and gs-HMQC spectroscopy were used for unambiguous correlation of ^{13}C chemical shifts and structure of TPPMS. Spin-lattice relaxation times T_1 were determined by the inversion recovery experiment. Crystallographic data were collected at 183(2) K with an Oxford Diffraction Xcalibur system with a ruby detector by using Mo-K_α radiation (λ = 0.7107 Å) that was graphite-monochromated. A suitable crystal was covered with oil (Infineum V8512, formerly known as Paratone N), mounted on top of a glass fibre and immediately transferred to the diffractometer. The program suite CrysAlisPro was used for data collection, semiempirical absorption correction and data reduction.[14] The structure was solved with direct methods by using SIR97[15] and refined by full-matrix least-squares methods on F_2 with SHELXL-97.[16] Two water molecules were disordered and refined with 50:50 and 55:45 occupancy, respectively. The hydrogen atoms of three water molecules could be localized and were refined with appropriate O–H distance restraints. The structure was checked for higher symmetry with help of the program Platon.[17] CCDC-748773 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Sodium (Diphenylphosphanyl)benzenesulfonate (1): Oleum (25 mL, 25% free SO_3) was placed in a 500-mL, three-necked flask charged with a 200-mL dropping funnel, and cooled in an ice bath to 0 °C. In order to get very good cooling conditions during the whole synthesis the ice bath was stirred magnetically and the reaction mixture was stirred mechanically with a KPG-stirring unit. Triphenylphosphane (10 g) was added in one step. The reaction mixture was cooled until all of the triphenylphosphane was dissolved (≈2 h). Then, the mixture was stirred at room temperature for 18 h. Then, the reaction mixture was cooled again to 0 °C, and water (150 mL) was added dropwise with very effective stirring to prevent local overheating. Using a pH-glass electrode and 7.5 M NaOH solution (ca. 130 mL) the mixture was neutralized. During neutralization, precipitation of the product as a white, fine solid was observed. This was filtered off at room temperature through a large glass filter funnel with no or only gentle suction. The white solid was transferred into an Erlenmeyer flask and recrystallized overnight from water (80 mL) at 4 °C to remove sodium sulfate impurities. The solid was filtered off, dried and suspended in *n*-pentane (50 mL) for several hours to extract unreacted starting material until the product was completely soluble in water. Yield 9.1 g (59%) of monosulfonated triphenylphosphane. ^1H NMR (200 MHz, D_2O, 25 °C): δ = 4.8 (s, water protons), 6,9–7.1 (m, 12 H), 7,6–7.8 (m, 2 H, 2-C and 4-C protons) ppm. $^{31}P\{^1H\}$ NMR (81 MHz, D_2O, 25 °C): δ = –5.7 (s) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, D_2O, 25 °C): δ = 140.6 (d, $^1J_{C,P}$ = 12.2 Hz, 1 C, 1-C), 132.8 (d, $^2J_{C,P}$ = 24.0 Hz, 1 C, 2-C), 145.8 (d, $^3J_{C,P}$ = 7.4 Hz, 1 C, 3-C), 128.6 (s, 1 C, 4-C), 131.7 (d, $^3J_{C,P}$ = 6.8 Hz, 1 C, 5-C), 138.1 (d, $^2J_{C,P}$ = 15.6 Hz, 1 C, 6-C), 138.2 (d, $^1J_{C,P}$ = 8.8 Hz, 2 C, 7-C), 136.2 (d, $^2J_{C,P}$ = 19.6 Hz, 4 C, 8-C), 131.3 (d, $^3J_{C,P}$ = 7.2 Hz, 4 C, 9-C), 131.8 (s, 2 C, 10-C) ppm.

(Diphenylphosphanyl)benzenesulfuric Acid (2): TPPMS^{Na} (**1**; 2.0 g) was dissolved in water (50 mL). The solution was transferred into a separating funnel and treated dropwise with concentrated hydrochloric acid solution (≈5.2 mL) until no additional milky emulsion was formed. The emulsion was chilled overnight, and the highly viscous lower phase was separated from the upper phase. Drying of the collected viscous oil resulted in a glassy, amorphous white solid, which was quickly pestled and vacuum dried again. The product was analyzed as TPPMS^H monohydrate. Yield: 70%. ^1H NMR (200 MHz, CD_3CN, 25 °C): δ = 5.6 (br. s, water/acid protons), 7,4–7.8 (m, 12 H), 7,9–8.1 (m, 2 H, C-SO_3-*ortho* protons) ppm. TPPMS^H is very hygroscopic, soluble in water, organic alcohols, acetone, acetonitrile and dichloromethane and insoluble in nonpolar organic solvents like hexane or toluene. Dimethyl sulfoxide causes oxidation of TPPMS^H.

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