Supporting Information

Stabilisation of water – soluble platinum nanoparticles by phosphonic acid derivatives

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Discussion of X-ray structures of 1, 3 and 4

Table S1: Crystal data and structure refinement for (**1**)$(MeOH)_2(H_2O)_2$, (**3**)$(H_2O)_4$, and (**4**)$_2(H_2O)_{17}$.

	(**1**)$(MeOH)_2$ $(H_2O)_2$	(**3**)$(H_2O)_4$	(**4**)$_2(H_2O)_{17}$
Empirical formula	$C_{16}H_{26}Na_2O_7P_2$	$C_{14}H_{22}Na_2O_8P_2$	$C_{42}H_{72}Na_4O_{23}P_2$
Formula weight	438.29	426.24	1098.90
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a [Å]	20.4328(3)	18.3578(18)	8.69271(16)
b [Å]	8.63377(13)	8.7338(7)	16.5739(3)
c [Å]	12.2755(2)	12.0390(15)	19.3218(4)
□ [°]	90	90	84.7890(16)
□ [°]	94.6314(15)	92.31(1)	78.4421(16)
□ [°]	90	90	83.8493(15)
V [Å^3]	2158.48(6)	1928.7(3)	2704.70(9)
Z	4	4	2
□$_{calc}$ [Mg/m^3]	1.349	1.468	1.349
Abs. [mm^{-1}]	0.274	0.308	0.189
Crystal size [mm^3]	0.43 x 0.34 x 0.03	0.33 x 0.12 x 0.03	0.52 x 0.28 x 0.09
Crystal descript.	colourless plate	colourless plate	colourless plate
Refl. obs.	4795	9318	10954
Completeness to theta	100.0 % to 30.51°	100.0 % to 28.28°	99.7 % to 30.50°
Max. and min. transmission	0.9918 and 0.9273	0.9908 and 0.9189	0.9832 and 0.8806
Data / restraints / param.	6589 / 2 / 264	14105 / 2 / 257	16465 / 0 / 744
GooF on F^2	1.003	0.991	0.965
Final R indices [*I*>2□(*I*)]	R_1 = 0.0343, wR_2 = 0.0842	R_1 = 0.0704, wR_2 = 0.1246	R_1 = 0.0419, wR_2 = 0.0941
R indices (all data)	R_1 = 0.0549, wR_2 = 0.0884	R_1 = 0.1168, wR_2 = 0.1381	R_1 = 0.0772, wR_2 = 0.1020
Elect. diff. [e·Å^{-3}]	0.427 / -0.241	0.874 / -0.593	0.425 / -0.304

The sodium salt **4** crystallized in the triclinic space group *P*-1. Its structure consists of two sodium phosphonate salts in the asymmetric unit together with 17 molecules of water. One of phosphonate anions binds to one sodium atom (Figure S1), the other forms only hydrogen bonds to water molecules, but does not directly coordinate to any cation. All oxygen atoms of the phosphonates are triple hydrogen-bond acceptors with the exception of O(41). This oxygen, which is coordinated to Na(4), additionally accepts two hydrogen bonds. The two phosphonate ligands are almost superimposable with a RSMD of only 0.0967 Å. The 4 sodium cations form together with one of the phosphonate anions and 13 out of the 17 water molecules an infinite two-dimensional cluster. Na(1) is octahedrally coordinated whereas Na(3) is in the centre of a square-pyramid. Na(2) and Na(4) are both similarly five-fold coordinated, their geometry looks like a transition state between a square pyramid and a trigonal bipyramid. The alternating hydrophobic and hydrophilic layers are oriented parallel to the a/b plane.

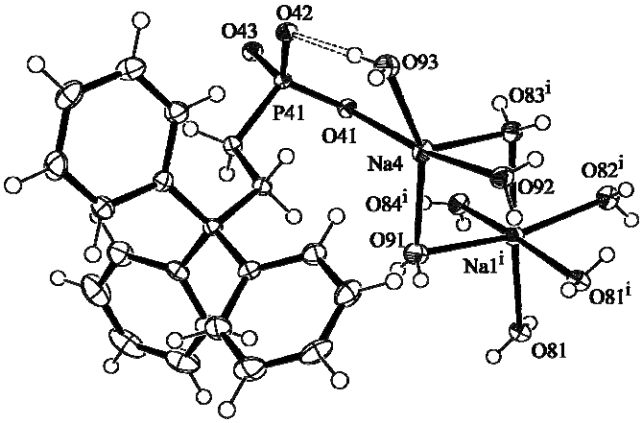

Fig. S1 ORTEP representation of one of the two triphenylpropylphosphonate molecules with two sodium cations (**4**) and eight water molecules at 50% probability. Symmetry operation i: -x,-y,-z-1.

The sodium salt **1** crystallized in the monoclinic space group $P2_1/c$ together with two molecules of methanol and water respectively. The phosphonate group coordinates asymmetrically with two oxygen atoms to Na(2), forming a four-membered chelate ring (Figure S2). Therefore the five-fold coordination sphere of Na(2) is strongly distorted and can neither be described as a square pyramid nor as a trigonal bipyramid. The other sodium ion, Na(1), forms a slightly distorted octahedron, coordinating to one phosphonate oxygen, two oxygen atoms of two methanol molecules and three water molecules. The latter all bridge two sodium cations. All these partners form an infinite two-dimensional cluster. The structural assembly is characterized by alternating hydrophobic and hydrophilic layers, which lay parallel to the b/c plane.

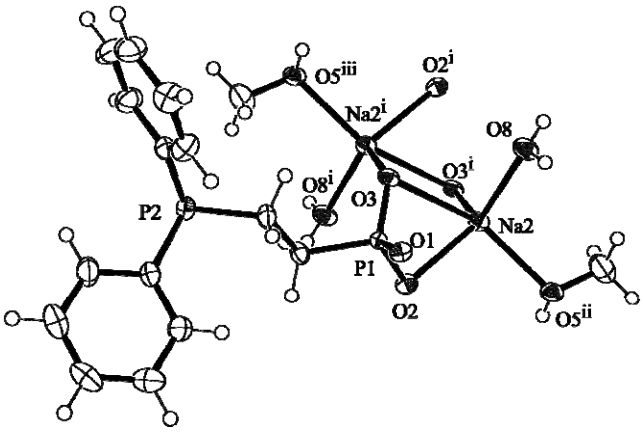

Fig. S2 ORTEP representation of a selected part of **1** at 50% probability. Symmetry operations i: -x,-y,-z-1; ii: -x,y+1/2,-z-1/2; iii: x,-y-1/2,z+-1/2.

The sodium salt **3** of the oxidized ligand of **1** crystallized in the monoclinic space group $P2_1/c$ together with four molecules of water. The phosphonate group again coordinates

asymmetrically with two oxygen atoms to a sodium cation (Na(11)), thereby forming a four-membered chelate ring (Figure S3). The other sodium, Na(12), forms a slightly distorted octahedron, coordinating to six water molecules. As in the structure of **1**, one oxygen atom of the phosphonate group bridges three sodium atoms. The oxygen of the phosphane oxide acts as a hydrogen bond acceptor from the water O(14). This does however not change the overall arrangement: the charged species form an infinite two-dimensional cluster, laying parallel to the b/c plane.

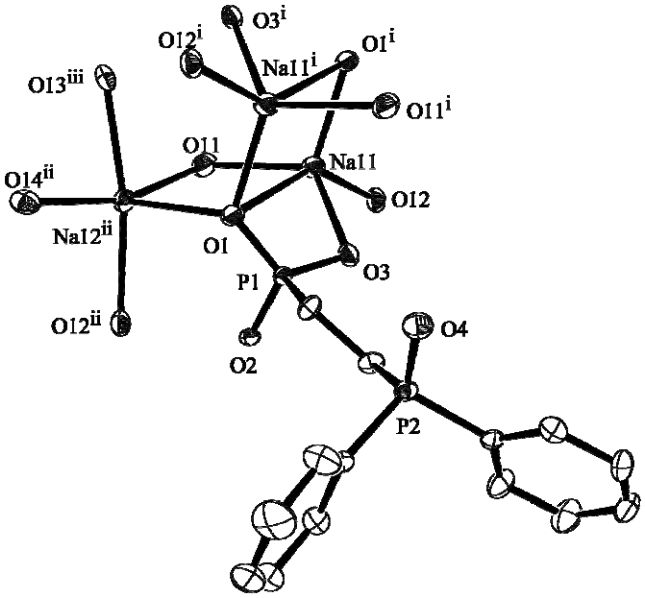

Fig. S3 ORTEP representation of the asymmetric unit of **3** plus some additional atoms at 50% probability. Hydrogen atoms were omitted for clarity. Symmetry operations i: 1-x,-y,1-z; ii: 1-x,-1/2+y,1/2-z; iii: x,-1/2-y,1/2+z.