Electronic Supplementary Information for Dalton Transactions
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Supporting Information

Sulfato-Bridged ECE-Pincer Palladium(II) Complexes: Structures in the Solid State and in Solution, and Catalytic Properties

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Hydrogen bonding in the structures. Water as lattice solvent is present in the crystals of both **3** and **4**. In **3** the sulfato oxygens O2 and O2a both accept a single hydrogen bond from water molecule O3 and O3a, respectively (Figure 4, Table 2). The second hydrogen atom of water O3 is disordered over two positions and donating to the symmetry related water O3c.

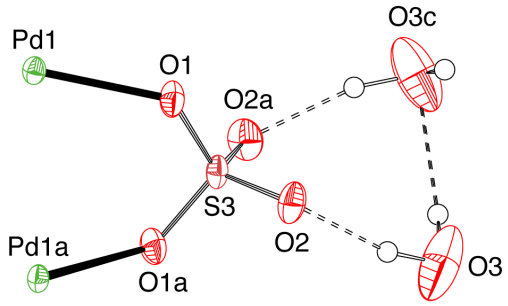

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Figure S1. Hydrogen bonding to **3** by two water molecules. Displacement ellipsoids are drawn at the 50% probability level. All C–H hydrogens and carbons are omitted for clarity. One of the hydrogen atoms in the water molecule is disordered; only one of the positions is shown.

Table S1: Selected hydrogen bond lengths (Å) and angles (deg) for **3**. Symmetry operation c: 1-x, y, 1/2-z.

Donor – H ··· Acceptor	D – H	H ··· A	D ··· A	D – H ··· A
O3 – H ··· O2	0.97	1.83	2.774(3)	166
O3 – H ··· O3c	0.97	2.15	3.020(4)	147

The asymmetric cell of **4** contains one molecule of **4** and six water molecules (Figure 5). The hydrogen-bonded water molecules and the non-coordinated oxygen atoms of the bridging sulfato ligand form two-dimensional sheets aligned in the crystallographic *a*,*c*-plane (Figure 6, showing the *a*,*b*-plane). The same hydrogen bonding motif can be found in **3**, *i.e.* two water molecules that are hydrogen bonded to the non-coordinated S=O oxygen atoms forming an eight membered ring. Each sulfato anion in the crystal structure of **4** accepts five moderately strong hydrogen bonds from five water molecules surrounding the sulfato moiety. The oxygen atoms coordinated to a Pd atom, O1 and O2, also accept one hydrogen bond from a water molecule, which are relatively the weakest among the observed hydrogen bonds (O31H···O1 length is 2.884(5) Å and O32H···O2 is 2.839(5) Å, see Table 3). Noteworthy is the strong hydrogen interaction O32H···O35d, indicated by the short bond distance (2.679(6) Å), which seems to compensate for the weaker hydrogen bond involving the O32 water atom (O32H···O2). The sixth water molecule is solely hydrogen bonded to other water molecules (O36) and is bridging the water molecules (O32 and O31) that are hydrogen bonded to the sulfates creating the two-dimensional sheets mentioned above. All the hydrogen bonds suggest a moderate to strong hydrogen bonding network of water molecules around the sulfato ligand, a property known for sulfato-metal containing compounds.[i] It must be noted that elemental analysis of **4** revealed the presence of only two equivalents of water molecules instead of the six found in the crystal structure. The sample prepared for elemental analysis, however, was exposed to high vacuum ($2.0 \cdot 10^{-7}$ mbar) at room temperature overnight.

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The fact that exactly two water molecules remain in the crystal lattice points at very strong hydrogen bonding of the remaining water molecules to the sulfato ligand in **4**.

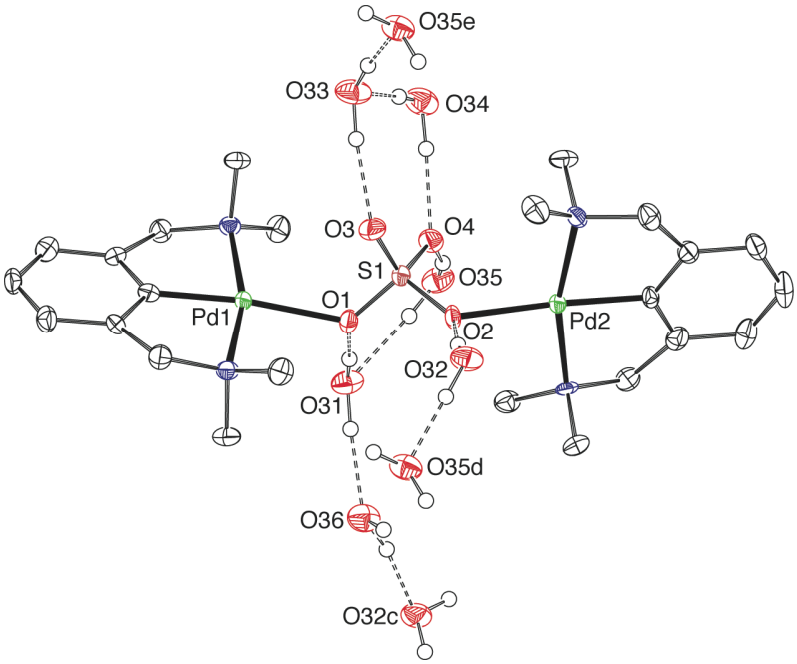

Figure S2. Hydrogen bonding around the bridging sulfato ligand in **4**. The C–H hydrogen atoms are omitted for clarity.

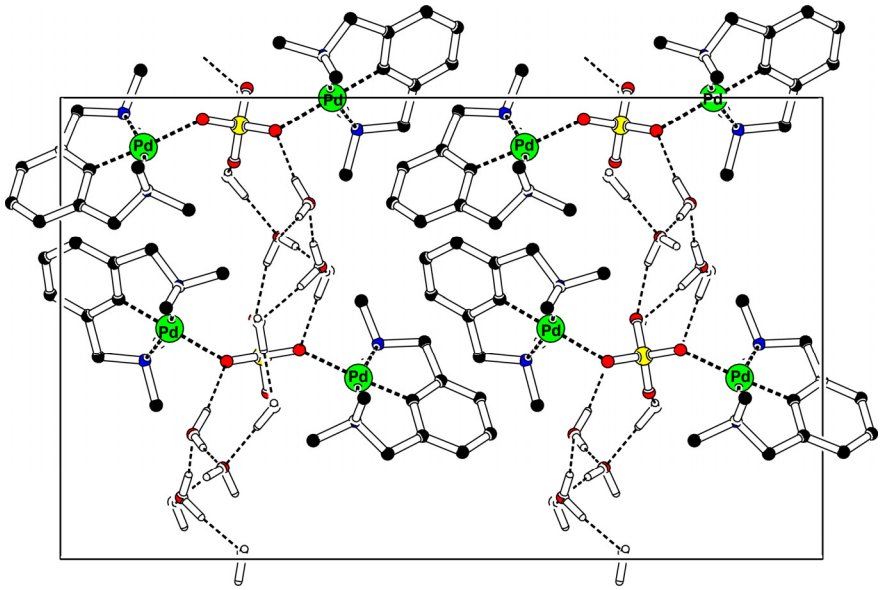

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Figure S3. View of the *a*,*b*-face of the infinite network hydrogen bonding in the crystal of **4**, forming two-dimensional sheets containing water molecules and sulfato ligands. The C–H hydrogen atoms are omitted for clarity.

Table S2: Selected hydrogen bond lengths (Å) and angles (deg) for **4**[a]. Symmetry operation d, e and f: ½+x, ½- y, ½+z. Symmetry operation g: 1+x, y, z.

Donor – H ··· Acceptor	D – H	H ··· A	D ··· A	D – H ··· A
O31 – H ··· O1	0.95	1.94	2.884(5)	173
O31 – H ··· O36	0.95	1.81	2.763(6)	172
O32 – H ··· O2	0.95	1.89	2.839(5)	172
O32 – H ··· O35d	0.95	1.73	2.679(6)	176
O33 – H ··· O3	0.95	1.84	2.789(6)	173
O33 – H ··· O35e	0.95	1.84	2.790(6)	170
O34 – H ··· O4	0.95	1.87	2.821(6)	172
O34 – H ··· O33	0.95	1.86	2.816(6)	177
O35 – H ··· O4	0.96	1.89	2.829(4)	165
O35 – H ··· O31	0.95	1.92	2.871(6)	174
O36 – H ··· O34f	0.96	1.83	2.781(6)	171
O36 – H ··· O32c	0.95	1.82	2.760(6)	170

[a] All hydrogen atoms are in calculated positions.

i. (a) Mahadevan Pillai, V. P.; Nayar, V.U.; Jordanovska, V. B. J. Solid State Chem. 1997, 133, 407-415.

(b) Damak, M.; Kamoun, M.; Daoud, A; Romain, F.; Lautie, A.; Novak, A. J. Mol. Struct. 1985, 130,

245-254.