

Electronic Supplementary Information for the paper: “Crystal structure of phosphonium carboxylate complexes. The role of the metal coordination geometry, ligand conformation and hydrogen bonding”

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SYNTHESIS OF COMPLEXES

Complex (1). To a solution of ZnCl₂ (68 mg, 0.5 mmol) in water (3 ml) at 80°C was added dropwise **L1** (334 mg, 1.0 mmol) in water (10 ml) at the same temperature. The stirring was continued for 15 min at 80°C. After 3 weeks at room temperature colorless crystals were separated, washed with water and ethanol and dried in *vacuo*. Complex **1** was obtained in 82.8% yield (332 mg). Mp 287.8°C. ³¹P NMR (CDCl₃, 161 MHz) δ28.4. IR (cm⁻¹, KBr): 1625s. Anal. Calc. for C₄₂H₅₂Cl₂O₁₁P₂Zn (%): C, 54.17; H, 5.59; P, 6.66. Found: C, 53.93; H, 5.34; P, 6.91.

Complex (2a). To a solution of ZnCl₂ (68 mg, 0.5 mmol) in water (3 ml) at 80°C was added dropwise **L2** (270 mg, 0.5 mmol) in water (10 ml) at the same temperature. The stirring was continued for 15 min at 80°C. After 3 weeks at room temperature colorless crystals were obtained, washed with water and ethanol and dried in *vacuo*. Crystals **2a** were obtained in 91.3% yield (308.5 mg). Mp 96.8°C. ³¹P NMR (CDCl₃, 161 MHz) δ26.27. IR (cm⁻¹, KBr): 1615s. Anal. Calc. for C₃₆H₄₄Cl₂O₆P₂Zn (%): C, 57.12; H, 4.95; P, 9.14. Found: C, 57.03; H, 5.08; P, 8.87.

Complex (2b). To a solution of HgCl₂ (135.8 mg, 0.5 mmol) in water (3 ml) at 80°C was added dropwise **L2** (270 mg, 0.5 mmol) in water (10 ml) at the same temperature. The stirring was continued for 15 min at 80°C. After 2 weeks at room temperature colorless crystals were obtained, washed with water and ethanol and dried in *vacuo*. Crystals **2b** were obtained in 74.7% yield (303 mg). Mp 135°C. ³¹P NMR (CDCl₃, 161 MHz) δ28.13. IR (cm⁻¹, KBr): 1620s. Anal. Calc. for C₃₆H₄₄Cl₂HgO₆P₂ (%): C, 49.71; H, 3.98; P, 7.32. Found: C, 49.73; H, 3.56; P, 7.27.

Complex (3). To a solution of CdCl₂ (91.7 mg, 0.5 mmol) in water (3 ml) at 80°C was added dropwise **L2** (270 mg, 0.5 mmol) in water (10 ml) at the same temperature. The stirring was continued for 15 min at 80°C. After 3 weeks at room temperature colorless crystals were obtained in 85.2% yield (308.1 mg). Mp 117°C. ³¹P NMR (CDCl₃, 161 MHz) δ27.17. IR (cm⁻¹, KBr): 1700s. Anal. Calc. for C₆₄H₆₆CdCl₄O₈P₄ (%): C, 46.02; H, 4.55; P, 7.43. Found: C, 45.78; H, 4.37; P, 7.23.

Complex (4). To a solution of salts CdCl₂ (91.7 mg, 0.5 mmol) and CuCl₂ (67.3 mg, 0.5 mmol) in water (10 ml) at 80°C was added dropwise **L1** (334 mg, 1.0 mmol) in water (10 ml) at the same temperature. The stirring was continued for 15 min at 80°C. After 3 weeks at room temperature green crystals were obtained in 64.0% yield (315.5 mg). Mp 250.7°C. ³¹P NMR (CDCl₃, 161 MHz) δ32.10. IR (cm⁻¹, KBr): 1625s. Anal. Calc. for C₈₄H₈₈Cd₂Cl₈Cu₂O₁₄P₄ (%): C, 50.70; H, 4.03; P, 6.15. Found: C, 51.33; H, 4.21; P, 6.01.

Complex (5). To a solution of salts CdCl₂ (91.7 mg, 0.5 mmol) and ZnCl₂ (68 mg, 0.5 mmol) in water (10 ml) at 80°C was added dropwise **L1** (334 mg, 1.0 mmol) in water (10 ml) at the same temperature. The stirring was continued for 15 min at 80°C. After 2 weeks at room temperature colorless crystals were obtained in 83.0% yield (430. mg). Mp 282.1°C. ³¹P NMR (CDCl₃, 161 MHz) δ27.13. IR (cm⁻¹, KBr): 1595s. Anal. Calc. for C₈₄H₇₆Cd₂Cl₈O₈P₂Zn₂ (%): C, 51.02; H, 3.85; P, 6.28. Found: C, 51.20; H, 3.80; P, 6.33.

Complex (6). To a solution of ZnCl₂ (68 mg, 0.5 mmol) in water (3 ml) at 80°C was added dropwise **L3** (174 mg, 0.5 mmol) in water (10 ml) at the same temperature. The stirring was continued for 15 min at 80°C. After 4 weeks at room temperature colorless crystals were separated, washed with water and dried in *vacuo*. Complex **6** was obtained in 82.6% yield (200 mg). Mp 127.7°C. ³¹P NMR (CDCl₃, 161 MHz) δ26.3. IR (cm⁻¹, KBr): 1565s. Anal. Calc. for C₂₂H₂₃Cl₂O₃PZn (%): C, 52.55; H, 4.58; P, 6.17. Found: C, 52.24; H, 4.81; P, 6.42.

Complex (7). To a solution of HgCl₂ (135.8 mg, 0.5 mmol) in water (3 ml) at 80°C was added dropwise **L3** (174 mg, 0.5 mmol) in water (10 ml) at the same temperature. The stirring was continued for 15 min at 80°C. After 4 weeks at room temperature colorless crystals were separated, washed with water and dried in *vacuo*. Complex **7** was obtained in 82.3% yield (255 mg). Mp 127.0°C. ³¹P NMR (CDCl₃, 161 MHz) δ30.15. IR (cm⁻¹, KBr): 1560s. Anal. Calc. for C₄₄H₄₂Cl₄Hg₂O₄P₂ (%): C, 42.61; H, 3.39; P, 5.00. Found: C, 42.31; H, 3.23; P, 5.09.

Complex (8). To a solution of CdCl₂ (91.7 mg, 0.5 mmol) in water (3 ml) at 80°C was added dropwise L4 (348 mg, 1 mmol) in water (10 ml) at the same temperature. The stirring was continued for 15 min at 80°C. After 3 weeks at room temperature colorless crystals were separated, washed with water and dried in *vacuo*. Complex 8 was obtained in 67.6% yield (370 mg). Mp 132.7°C. ³¹P NMR (CDCl₃, 161 MHz) δ29.48. IR (cm⁻¹, KBr): 1565s. Anal. Calc. for C₄₄H₅₀CdCl₂O₈P₂ (%): C, 55.50; H, 5.26; P, 6.52. Found: C, 55.87; H, 4.83; P, 6.81.

Complexes (9, 10). To a solution of ZnCl₂ (68.2 mg, 0.5 mmol) in water (3 ml) at 80°C was added dropwise L4 (348 mg, 1 mmol) in water (10 ml) at the same temperature. The stirring was continued for 15 min at 80°C. After 4 weeks at room temperature colorless crystals were separated, washed with water and dried in *vacuo*. Complexes 9 and 10 were obtained in 84% yield (350 mg). Mp 106.2°C (complex 9) and 181.4 (complex 10). ³¹P NMR (CDCl₃, 161 MHz) δ28.1 (9), 32.1 (10). IR (cm⁻¹, KBr): 1570s and 1630s.

Complex (11). To a solution of CdCl₂ (91.7 mg, 0.5 mmol) in water (3 ml) at 80°C was added dropwise L5 (410 mg, 1 mmol) in water (15 ml) at the same temperature. The stirring was continued for 15 min at 80°C. After 4 weeks at room temperature colorless crystals were separated, washed with water and dried in *vacuo*. Complex 11 was obtained in 44.5% yield (224 mg). Mp 151.7°C. ³¹P NMR (CDCl₃, 161 MHz) δ27.27. IR (cm⁻¹, KBr): 1630s. Anal. Calc. for C₅₄H₅₀CdCl₂O₈P₂ (%): C, 62.34; H, 4.43; P, 5.96. Found: C, 62.37; H, 4.87; P, 6.31.

Complex (12). To a solution of CuCl₂ (67.2 mg, 0.5 mmol) in water (3 ml) at 80°C was added dropwise L5 (410 mg, 1 mmol) in water (15 ml) at the same temperature. The stirring was continued for 15 min at 80°C. After 2 weeks at room temperature green crystal were separated, washed with water and dried in *vacuo*. Complex 12 was obtained in 47.6% yield (227 mg). Mp 131.7°C. ³¹P NMR (CDCl₃, 161 MHz) δ24.30. IR (cm⁻¹, KBr): 1625s, 1560s. Anal. Calc. for C₁₂₆H₁₂₄Cl₂Cu₂O₂₁P₄ (%): C, 67.80; H, 5.11; P, 5.82. Found: C, 67.52; H, 5.27; P, 5.98.

CRYSTALLOGRAPHY. DETAILS OF THE REFINEMENT

COMPLEX 1 – CCDC 927945. Besides the molecule of the complex, the unit cell contains 7 water molecules in the asymmetric unit, solvate water hydrogens were located from the difference Fourier map and refined isotropically, two water molecules being refined with geometrical constraints.

COMPLEX 2A – CCDC 964968. The crystals 2a and 2b are isomorphous. The crystal structure was solved and refined in monoclinic space group C2/c, β-angle being equal 90.2°. The symmetry check using equivalent reflections gave the value of R(sym)=0.53 for orthorhombic system and 0.03 for monoclinic system. The molecule is in a special position on a two-fold axis, both phenyl rings are disordered over two positions with the occupation ratio 0.7:0.3 for both of them and refined with geometrical constraints. The crystal contains one solvate ethanol molecule in the asymmetric part of the unit cell, which forms a strong hydrogen bond with the carbonyl oxygen atom with the following parameters O17-H17...O2, O17-H17 0.82 Å, H17...O2 1.91 Å, O2...O17 2.69 Å, ∠O17-H17...O2 158.5°.

COMPLEX 2B – CCDC 927938. The crystal 2b is isomorphous to 2a. The crystal structure was solved and refined in monoclinic space group C2/c, monoclinic angle being equal 90.0°. The symmetry check using equivalent reflections gave the value of R(sym)=0.32 for orthorhombic system and 0.04 for monoclinic system, moreover it was impossible to solve the structure in orthorhombic space groups. The molecule is in a special position on a two-fold axis, both phenyl rings are disordered over two positions with the occupation ratio 0.7:0.3 for both of them and refined with geometrical constraints. One peak of the rest electron density 1.37 e/Å³ is located in the vicinity of metal ion. The crystal contains one solvate ethanol molecule in the asymmetric part of the unit cell, which forms a strong hydrogen bond with the carbonyl oxygen atom with the following parameters O17-H17...O2, O17-H17 0.84 Å, H17...O2 1.89 Å, O2...O17 2.70 Å, ∠O17-H17...O2 161.2°.

COMPLEX 3 – CCDC927940. The cation is in a special position on a two-fold axis and bears the charge of +1, with one carboxyl group being deprotonated, while the second is not. However only one half of the ligand is in the asymmetric unit, thus, the hydrogen atom was refined with half occupancy. It was located from a difference Fourier map and refined isotropically resulting in the position equidistant from two oxygen atoms from the neighbouring cations, which are very close to each other: O...O 2.42 Å. The ratio of the ligand cation to CdCl₄²⁻ anion is 2:1.

COMPLEX 4 – CCDC927937. The molecule is in a special position, both Cu and Cd atoms occupy 4i Wyckoff positions. Besides the coordinated water molecules two solvate water molecules were located in the asymmetric part of the unit cell from the difference Fourier map and refined anisotropically, one with full occupancy, the other disordered over two positions. Hydrogens atoms were also found from the difference Fourier map and refined with geometrical constraints. No other significant rest electron density peaks were found although the program “Platon” [1] indicates a solvent accessible void of 159 Å³, most probably filled with disordered water molecules. The disorder accounts for the low ratio of observed reflections, which gives alert B in checkCif report.

COMPLEX 5 – CCDC 927944. The crystal contains channel voids filled with disordered water molecules along the b-axis. The expected volume for solvent molecules as estimated using the program “Platon” [1] is about 460 Å³ per unit cell volume. As it often happens with channels filled with solvents, it was impossible to find a reasonable model for solvate water in the channels, thus the ‘Squeeze’ option of “Platon” was applied to obtain solvent-free reflection file which was further used for the refinement.

COMPLEX 6 – CCDC927941. All hydrogen atoms were placed into calculated positions except coordinated water molecule, these hydrogen atoms being located from the difference Fourier map. All of them were refined using the riding model, for water molecule using AFIX 3 mode.

COMPLEX 7 – CCDC927942. The molecule is in a special position in the inversion center. The methyl group is disordered over two positions with the occupancy 0.75:0.25.

COMPLEX 8 – CCDC 927939. The crystal contains solvate water molecules: in the asymmetric part of the unit cell 3 water molecules with full occupancy and one water molecule disordered over two sites with half-occupancy. Hydrogen atoms of water molecules were revealed from the difference Fourier map and then refined as riding atoms using AFIX3 constrain, while the hydrogen atoms of two water molecules were refined using geometrical constrains on OH bond lengths and H...H distances. One of the water molecules with partial occupancy gives alert B – “no hydrogen bonding for hydrogen atom”, however no other possible hydrogen positions could be reliably refined. The crystal was weakly diffracting at higher angles due to disorder, thus the completeness of the data set is 96% up to $\theta=25^\circ$.

COMPLEX 9 – CCDC 927943. The crystal **9** is a thin plate with the ratio of reflections greater than $I > 2\sigma(I)$ only 42% due to disorder. The asymmetric part of the unit cell contains two independent molecules of the complex and disordered water molecules, one with full occupancy and 6 sites half-populated. Thus, it appeared impossible to locate hydrogen atoms from the difference Fourier map, their positions were calculated using XHYDEX program incorporated into WinGX package [2] and refined as riding atoms using AFIX 3 constrain. All water molecules are at the ‘hydrogen-bond’ distance with the oxygen atoms of the complex, the neighboring water molecules, or chlorine atoms. Room-temperature data and disorder of solvate water molecules did not allow locating hydrogen atoms more reliably.

COMPLEX 10 – CCDC 927936. Complex 10 gave poor quality twinned crystals. The unit cell was determined using “Cell_now” program, the data was processed as a two-domain twinned crystal with a twin law (-0.997, 0.001, 0.006/0.000, -1.000, 0.002/1.153, -0.009, 0.997). The structure was refined using “hklf 5” data file composed of corrected reflections from both domains, obtained after scaling and absorption correction using “Twinabs” program, $R_{int} = 0.0979$ for all 52894 observations and $R_{int} = 0.0401$ for all 10138 observations with $I > 3\sigma(I)$. Both programs “Cell_now” and “Twinabs” are incorporated into APEX2 package [3]. Two peaks in electron density difference map slightly larger than 1 e are located near metal atoms, two other peaks were modeled as a disordered water molecule with half occupancy, hydrogen atoms were impossible to locate. The level B alert in checkcif report is a false alert originating from the two-domain data set, the same reason accounts for large discrepancy between calculated and reported T_{min} , T_{max} transmission coefficients.

COMPLEX 11 – CCDC 927946. The molecule of the complex is in a special position on a 2-fold axis. The crystal contains solvate disordered water molecules. The two water molecules per complex were modeled as disordered over 4 positions, one half populated, oxygen atoms being refined anisotropically, the rest three positions with occupancy 0.25, 0.125, 0.125 were refined isotropically. Hydrogen atoms were not found, but were taken into account in the sum formula, which resulted in two alerts C indicating discrepancy between calculated and reported formula and $F(000)$.

COMPLEX 12 – CCDC 927947. The crystal is composed of the copper containing cation with the charge 2^+ , which is in a special position in the centre of symmetry, two chlorine counter anions and 9 solvate water molecules per cation. Three water molecules in the asymmetric part have the occupancy of 0.5 and three sites are fully occupied. In spite of the room temperature measurement it appeared to be possible to find hydrogen atoms attached to 4 water molecules and to refine them with geometrical constraints. For two half-populated water molecules it was impossible to locate hydrogens, which results in alerts C: “calc. and reported SumFormula strings differ”, “reported $F000$ differs from calcd”. The cinnamic acid residue coordinating copper atoms is disordered over two positions with nearly equal (0.46) occupancy.

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