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# Electronic Supporting Information

## Models to Predict the Magnetic Properties of Single- and Multiple-Bridged Phosphate $Cu^{II}$ Systems: A Theoretical DFT Insight.

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**Table S1.** Selected structural parameters Cu-O-P angle (º), Cu-O-Cu angle (°), Cu-O-O-Cu and D-P-O-Cu dihedral angles (º) related to the REFCODE of each studied compound. The coordination number (CN) of the $Cu^{II}$ ions and type of ligand are also included.

| Compound | REFCODE | CN of $Cu^{II}$ centers | Phosphate bridges | Phosphate-coordination | (Cu-O-P) | (Cu-O-O-Cu) | (Cu-O-Cu) | (D-P-O-Cu) (□) |
|---|---|---|---|---|---|---|---|---|
| 1 | IKUVUF | 5 | 2 $H_2PO_4^-$ | 1,3- $H_2PO_4^-$ | 135.1 (1); 135.1 (1) | -41.4(2) | --- | 60.32; 121.81 |
| | | | | 1,3- $H_2PO_4^-$ | 135.1 (1); 135.1 (1) | 41.4(2) | --- | |
| 2 | LEJLUI1 | 5 | 2 $H_2PO_4^-$ | 1,3- $H_2PO_4^-$ | 131.5 (2); 133.5 (2) | -38.7(4) | --- | 59.00; 115.21 |
| | | | | 1,3- $H_2PO_4^-$ | 133.5 (2); 131.5 (2) | 38.7(4) | --- | |
| 3 | MADVIX | 5 | 2 $H_2PO_4^-$ | 1,3- $H_2PO_4^-$ | 130.9 (7); 134.3 (8) | 57.1(1) | --- | 51.95; 127.12 |
| | | | | 1,3- $H_2PO_4^-$ | 134.3 (8); 130.9 (7) | -57.1(1) | --- | |
| 4 | LEJLUI2 | 5 | 2 $H_2PO_4^-$ | 1,3- $H_2PO_4^-$ | 127.0 (2); 129.2 (2) | 5.1(2) | --- | 155.28; 161.37 |
| | | | 1 $HPO_4$ | 1,1- $HPO_4^{2-}$ | --- | --- | 92.8 (1) | --- |
| | | | | 1,1- $H_2PO_4^-$ | --- | --- | 94.0 (1) | --- |
| 5 | RONBOL | 5 | 2 $H_2PO_4^-$ | 1,1- $H_2PO_4^-$ | --- | --- | 97.2 (9) | --- |
| | | | | 1,1- $H_2PO_4^-$ | --- | --- | 97.2 (9) | --- |
| 6 | EMEWEY | 5 | 2 $HPO_4^{2-}$ | 1,1- $HPO_4^{2-}$ | --- | --- | 93.0 (1) | --- |
| | | | | 1,1- $HPO_4^{2-}$ | --- | --- | 93.0 (1) | --- |
| 7 | PENTUZ | 5 | $HPO_4^{2-}$ | 1,3- $HPO_4^{2-}$ | 128.9(1) | -112.2(4) | --- | 0.67; 109.99 |
| 8 | PUCHIE | 5 | $PO_4^{2-}$ | 1,3- $PO_4^{3-}$ | 135.6(1); 135.6(1) | -89.3(6) | --- | 19.64; 219.36 |
| | PUCHIE | | | 1,3- $PO_4^{3-}$ | 135.6(1); 135.6(1) | -107.7(2) | | 99.83; 260.17 |
| 9 | WABSOI | 5 | $PO_4^{2-}$ | 1,3- $PO_4^{3-}$ | 120.9(2); 129.5(2) | 78.1(4) | --- | 13.97; 76.19 |
| | | | | 1,3- $PO_4^{3-}$ | 126.9(2); 128.4(2) | -143.8(3) | --- | 34.30; 221.44 |
| | | | | 1,3- $PO_4^{3-}$ | 126.9(2); 129.(2) | 168.8(2) | --- | 46.76; 277.61 |
| | | | | 1,3- $PO_4^{3-}$ | 120.9(2); 128.4(2) | -101.5(5) | --- | 14.58; 134.80 |
| | | | | 1,3- $PO_4^{3-}$-other* | 120.9(2); 126.9(2) | 67.7(2) | --- | 162.61; 106.98 |
| | | | | 1,3- $PO_4^{3-}$-other* | 128.4(2); 129.5(2) | -79.4(1) | --- | 156.32; 104.40 |
| 10 | FIBKAD | 6 – 5 | 2 $HPO_4^{2-}$ | 1,3- $H_2PO_4^-$ | 135.6(1); 130.0(1) | 91.6(1) | --- | 100.59; 226.91 |
| | | | | 1,3- $H_2PO_4^-$ | 135.6(1); 84.6(1) | 121.6(7) | --- | 19.89; 183.92 |
| | | | | 1,1- $H_2PO_4^-$ | --- | ---- | 137.7(1) | --- |
| | | | | 1,3- $H_2PO_4^-$ | 84.6(1); 130.0(1) | -58.8(1) | --- | 61.20; 145.90 |
| | | | | 1,3- $H_2PO_4^-$ | 105.0(1); 130.0(1) | 80.5(1) | --- | 62.04; 100.59 |
| 11 | PUJNEN | 4 – 5 | 2 $H_2PO_4^-$ | 1,3- $H_2PO_4^-$ | 134.3(2); 146.9(3) | -76.4(5) | --- | 56.56; 195.22 |
| | | | | Not phosphate† | | | --- | |
| | | | | Not phosphate§ | | | --- | |

* Pyrazole ; †pyridine-2-aldehyde thiosemicarbazone ; § bis(pyridine-2-aldehyde) thiocarbohydrazone

Figure S1. a) A side view of the (0°,0°) model (above) and the view through the Cu-O vectors showing their collinearity (below). b) A side view of the (90°, 270°) model (above) and the eclipsed view of the P-O vectors (below). Green: dummy atom; dark blue: nitrogen from the amine ligands; red: oxygen, yellow: phosphorus and white: hydrogen atoms.

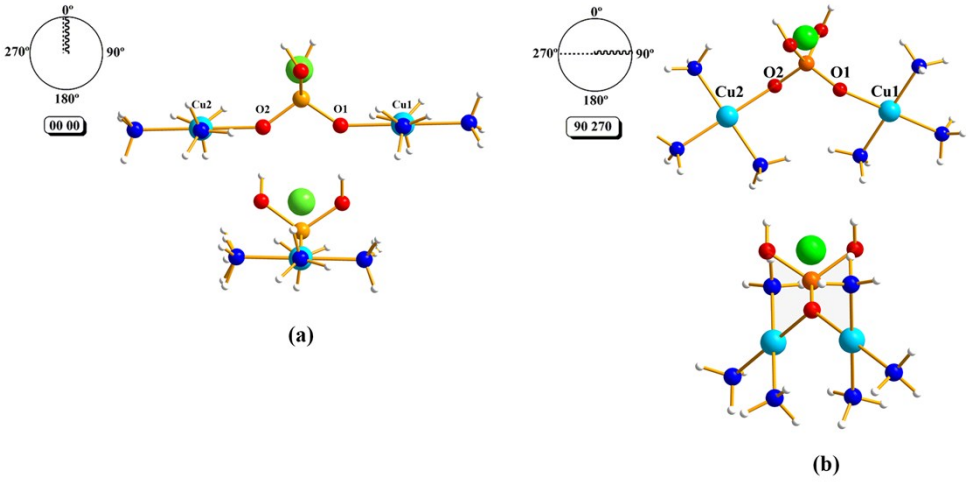

Figure S2. Virtual cones produced by the scanning of the dihedral angles D-P-O-Cu by moving both Cu-O vectors. Left: Cu-O bonds forming the virtual cones. The black arrow in the phosphorus atom represents the P-Dummy vector, which is the intersection between the planes O1-P-O2 and O3-P-O4.