## Supporting Information

# Co-sensitization Promoted Light Harvesting with a New Mixed-Addenda Polyoxometalate $[Cu(C_{12}H_8N_2)_2]_2[V_2W_4O_{19}]\cdot 4H_2O$ in Dye-Sensitized Solar Cells

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**Table S1** Bond Valence Sums

| bond | bond -length | bond-dist | [exp[($r_0$-r)/B] | BVS=Σexp[($r_0$ - r) /B] |
|---|---|---|---|---|
| W(1)-O(2) | 1.91 | 1.96 | 0.873 | 6.259 |
| W(1)-O(3) | 1.91 | 2.296 | 0.351 | |
| W(1)- | 1.91 | 1.875 | 1.099 | |
| W(1)-O(7) | 1.91 | 1.974 | 0.841 | |
| W(1)-O(8) | 1.91 | 1.661 | 1.960 | |
| W(1)-O(9) | 1.91 | 1.863 | 1.135 | |

| bond | bond -length | bond-dist | [exp[($r_0$-r)/B] | BVS=Σexp[($r_0$ - r) /B] |
|---|---|---|---|---|
| W(2)-O(1) | 1.91 | 1.894 | 1.044 | 6.252 |
| W(2)-O(3) | 1.91 | 2.314 | 0.335 | |
| W(2)-O(4)#1 | 1.91 | 1.928 | 0.952 | |
| W(2)-O(7)#1 | 1.91 | 1.956 | 0.883 | |
| W(2)-O(9) | 1.91 | 1.895 | 1.041 | |
| W(2)-O(10) | 1.91 | 1.654 | 1.997 | |

| bond | bond -length | bond-dist | [exp[($r_0$-r)/B] | BVS=Σexp[($r_0$ - r) /B] |
|---|---|---|---|---|
| W(3)-O(1) | 1.91 | 1.917 | 0.981 | 6.051 |
| W(3)-O(2) | 1.91 | 1.886 | 1.067 | |
| W(3)-O(3) | 1.91 | 2.285 | 0.363 | |
| W(3)-O(4) | 1.91 | 1.889 | 1.058 | |
| W(3)-O(5) | 1.91 | 1.943 | 0.915 | |
| W(3)-O(6) | 1.91 | 1.721 | 1.667 | |

| bond | bond -length | bond-dist | [exp[($r_0$-r)/B] | BVS=Σexp[($r_0$ - r) /B] |
|---|---|---|---|---|
| V(1)-O(2) | 1.803 | 1.96 | 0.65 | 4.689 |
| V(1)-O(3) | 1.803 | 2.296 | 0.263 | |
| V(1)-O(5)#1 | 1.803 | 1.875 | 0.823 | |
| V(1)-O(7) | 1.803 | 1.974 | 0.630 | |
| V(1)-O(8) | 1.803 | 1.661 | 1.468 | |
| V(1)-O(9) | 1.803 | 1.863 | 0.850 | |

| bond | bond -length | bond-dist | [exp[($r_0$-r)/B] | BVS=Σexp[($r_0$ - r) /B] |
|---|---|---|---|---|
| V(2)-O(1) | 1.803 | 1.894 | 0.782 | 4.683 |
| V(2)-O(3) | 1.803 | 2.314 | 0.251 | |
| V(2)-O(4)#1 | 1.803 | 1.928 | 0.713 | |
| V(2)-O(7)#1 | 1.803 | 1.956 | 0.661 | |
| V(2)-O(9) | 1.803 | 1.895 | 0.780 | |
| V(2)-O(10) | 1.803 | 1.654 | 1.496 | |

| bond | bond -length | bond-dist | [exp[($r_0$-r)/B] | BVS=Σexp[($r_0$ - r) /B] |
|---|---|---|---|---|
| Cu(1)-N(1) | 1.763 | 2.115 | 0.386 | |
| Cu(1)-N(2) | 1.763 | 1.977 | 0.561 | |
| Cu(1)-N(3) | 1.763 | 2.088 | 0.415 | 2.339 |
| Cu(1)-N(4) | 1.763 | 1.960 | 0.587 | |
| Cu(1)-O(7) | 1.679 | 2.027 | 0.390 | |

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,-y+1/2,-z+1

**Table S2** Comparison of M-O average bond distances of compound **1** with those in reported cluster anions.

| anion | M-$O_c$(Å) | M-$O_b$(Å) | M-$O_t$ (Å) |
|---|---|---|---|
| $[W_6O_{19}]^{2-}$ | 2.331 | 1.922 | 1.694 |
| $[V_2W_4O_{19}]^{4-}$ | 2.305 | 1.922 | 1.695 |
| **1** | 2.299 | 1.915 | 1.679 |

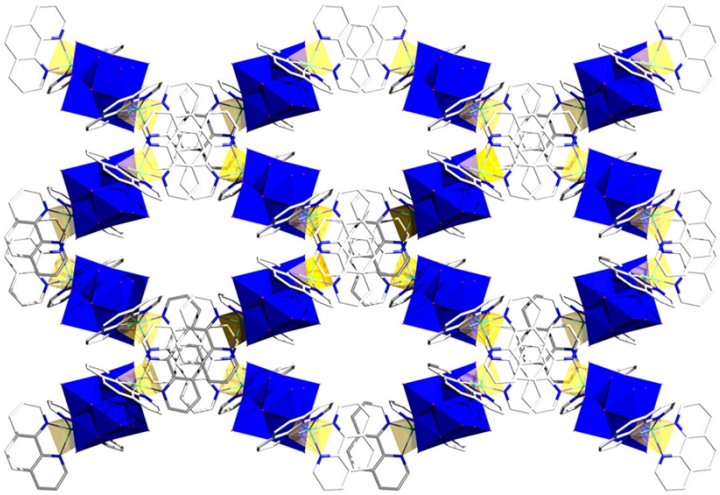

**Fig. S1** Packing arrangement of **1** viewed along c axis. The polyanions are represented with polyhedra: {$CuON_4$}, yellow polyhedron; {W(V)$O_6$}, blue octahedron; C (grey) and N (blue) ions are shown with thick sticks.

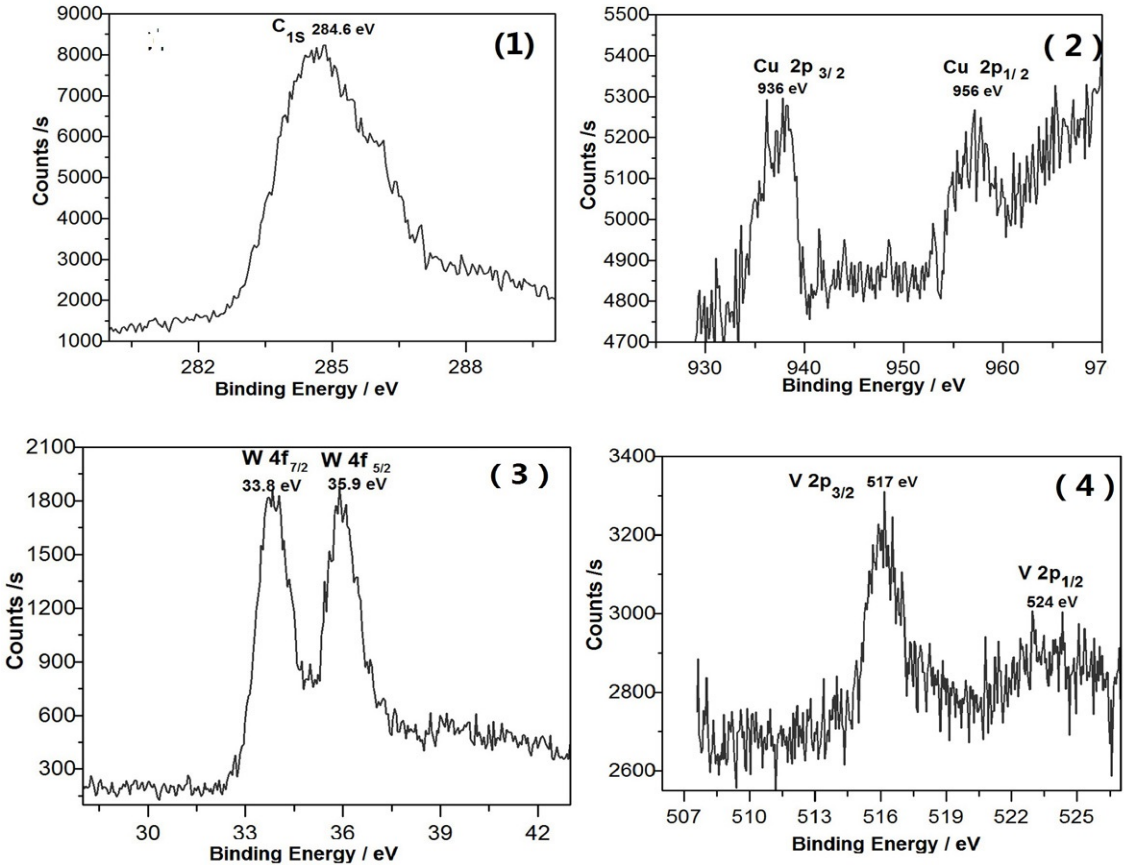


**Fig. S2** The XPS spectra of C1s(1), Cu2p(2), W4f(3), V2p(4)

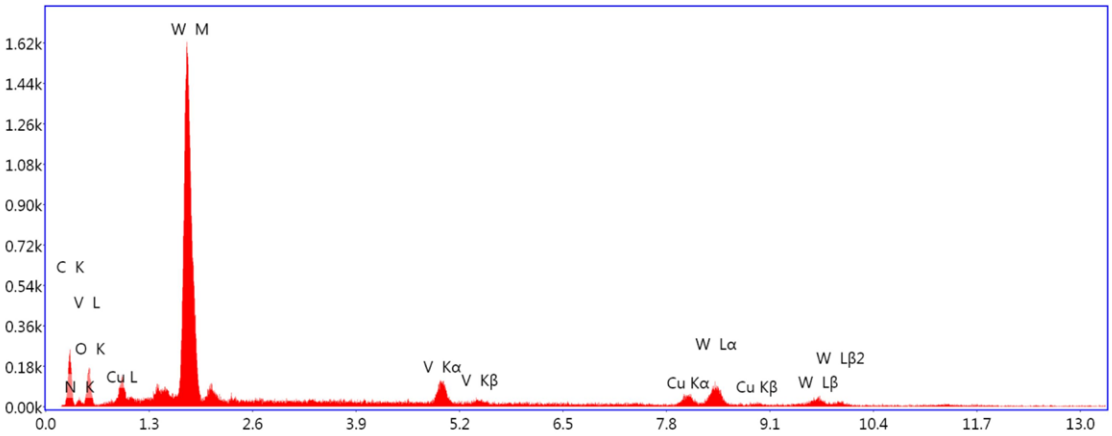


**Fig. S3** The EDX diagram of **1**

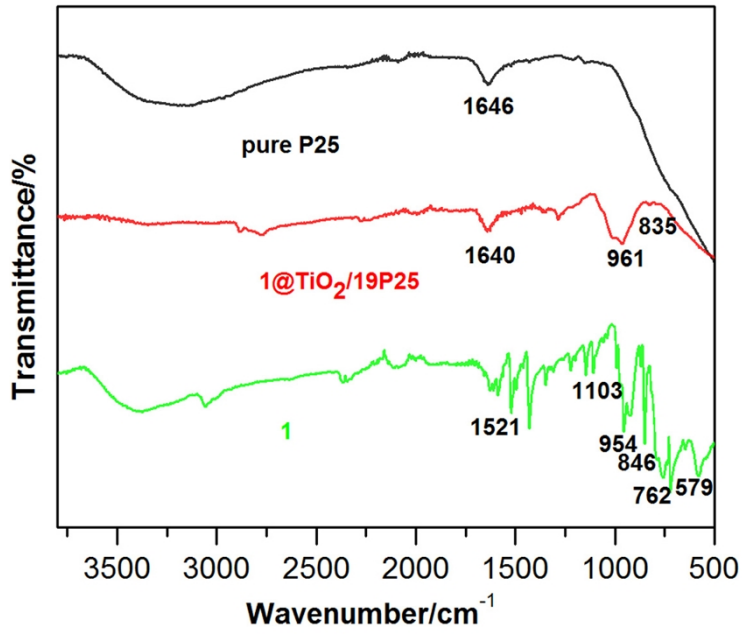


**Fig. S4** The FT-IR spectra of **1**(green), **1**@$TiO_2$/19P25(red) and pure P25(black)

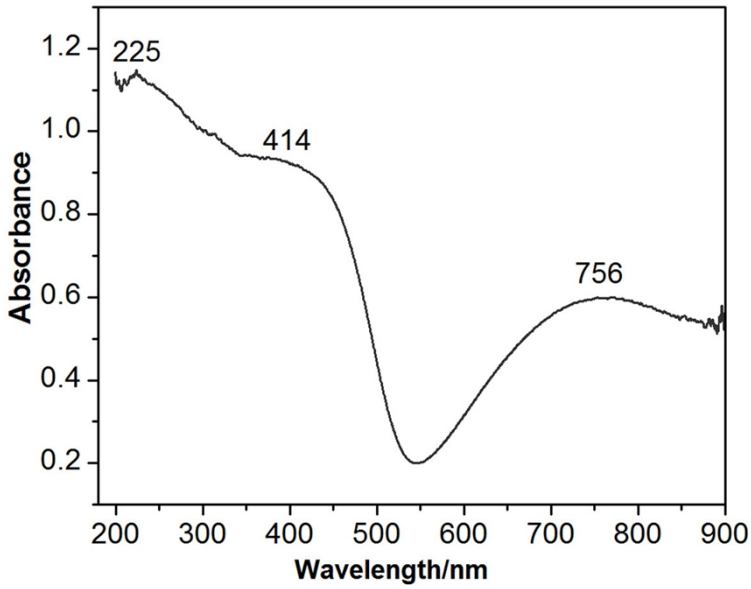


**Fig. S5** The UV-Vis spectrum of **1**

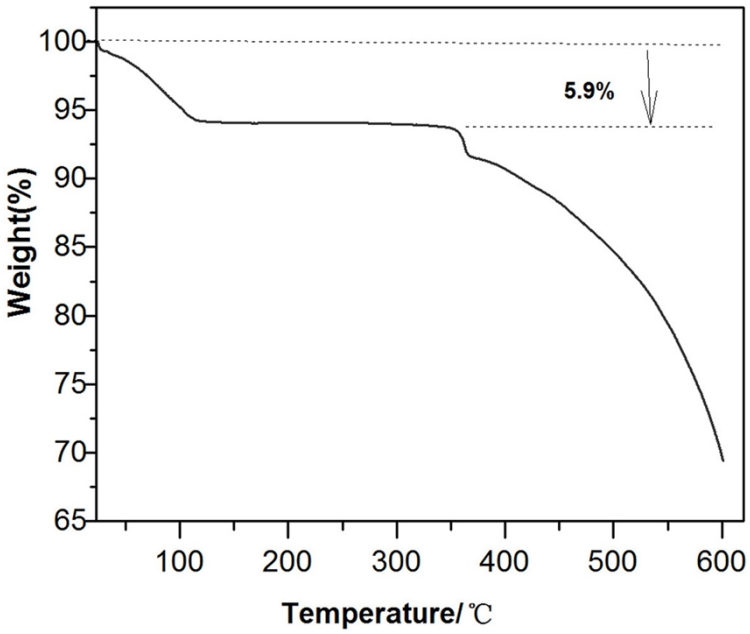


**Fig. S6** Thermogravimetric analysis (TGA) curve of **1**

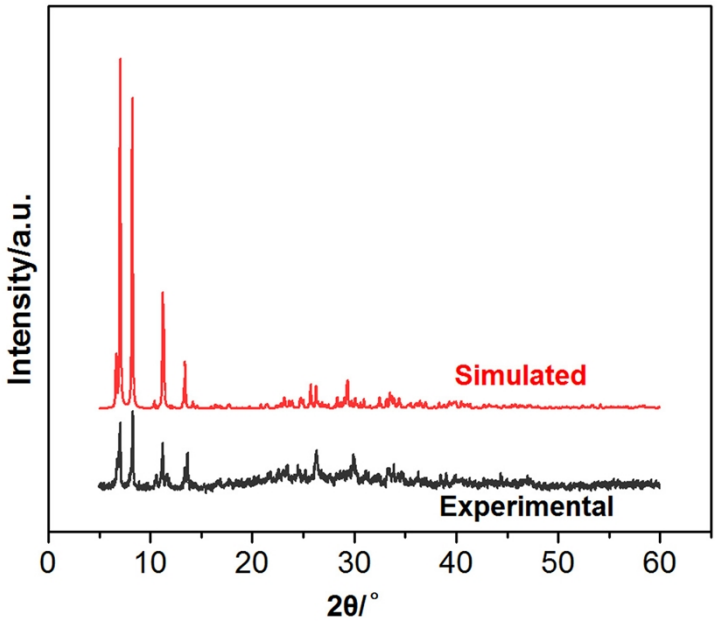


**Fig. S7** The simulated and measured XRD patterns of **1**

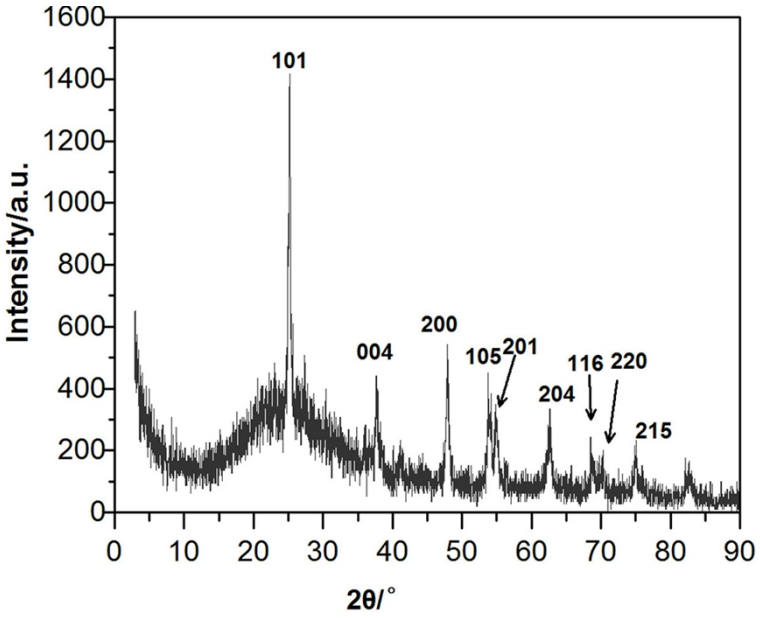


**Fig. S8** XRD pattern of the **1**@$TiO_2$/19P25 composite

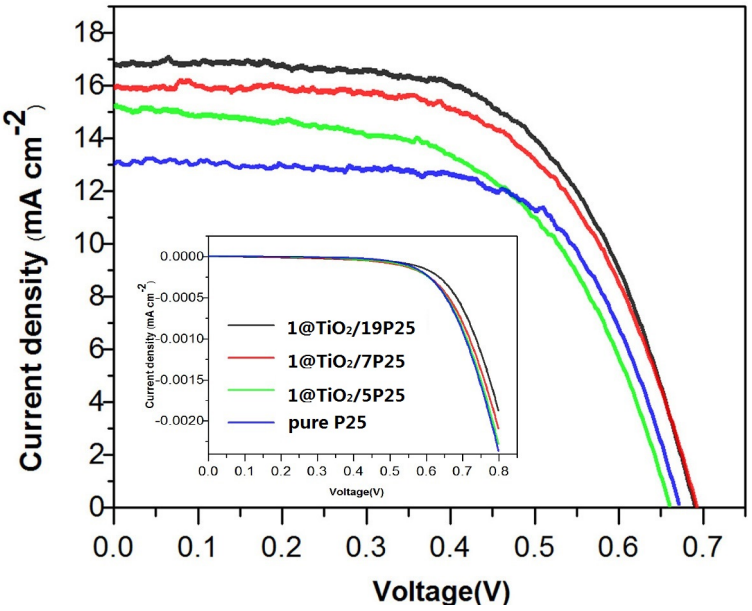


**Fig. S9** The current voltage curves of DSSCs with **1**@$TiO_2$/nP25 (n=5, 7, 19) and pure P25 electrode under AM 1.5 radiation (100 mW $cm^{-2}$). The inset is the current voltage curves under dark condition.

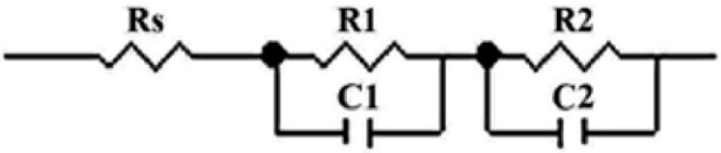


**Fig. S10** Equivalent circuit used to fit the impedance measurements on the DSSCs

**Table S3** Fitted parameters and electron lifetime calculated from $f_{max}$

| Sample | $Rs(\Omega)$ | $R_1(\Omega)$ | $R_2(\Omega)$ | $f_{max}$(Hz) | $\tau_e$ (ms) |
|---|---|---|---|---|---|
| N719 | 33.2 | 37.9 | 5.83 | 56.3 | 2.83 |
| **1**/N719 | 27. 1 | 34.9 | 5.17 | 27.7 | 5.75 |

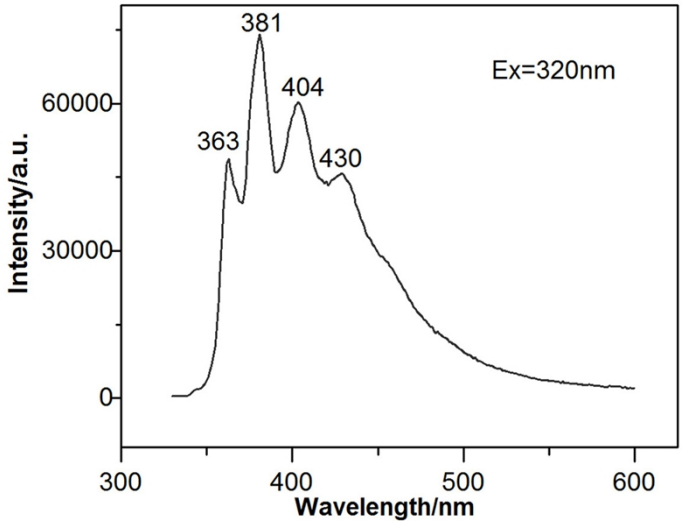


**Fig. S11** The emission spectrum (*Ex*= 320 nm) of the phen

**Table S4** Selected bond lengths (Å) and bond angles (°) of **1**

| | | | |
|---|---|---|---|
| W(1)/V(1)-O(2) | 1.961 | W(3) -O(1) | 1.917 |
| W(1)/V(1)-O(3) | 2.296 | W(3)-O(2) | 1.886 |
| W(1)/V(1)-O(5)#1 | 1.875 | W(3) -O(3) | 2.285 |
| W(1)/V(1)-O(7) | 1.974 | W(3) -O(4) | 1.889 |
| W(1)/V(1)-O(8) | 1.661 | W(3) -O(5) | 1.943 |
| W(1)/V(1)-O(9) | 1.863 | W(3) -O(6) | 1.721 |
| W(2)/V(2)-O(1) | 1.894 | Cu(1)-N(1) | 2.115 |
| W(2)/V(2)-O(3) | 2.314 | Cu(1)-N(2) | 1.977 |
| W(2)/V(2)-O(4)#1 | 1.928 | Cu(1)-N(3) | 2.088 |
| W(2)/V(2)-O(7)#1 | 1.956 | Cu(1)-N(4) | 1.960 |
| W(2)/V(2)-O(9) | 1.895 | Cu(1)-O(7) | 2.027 |
| W(2)/V(2)-O(10) | 1.654 | | |
| N(1)-C(1) | 1.332(18) | N(2)-C(12) | 1.315(19) |
| N(1)-C(5) | 1.369(18) | N(2)-C(7) | 1.361(19) |
| N(3)-C(13) | 1.323(18) | N(4)-C(24) | 1.341(17) |
| N(3)-C(17) | 1.364(18) | N(4)-C(18) | 1.380(17) |
| O(8)-W(1)-O(2) | 102.9(4) | O(1)-W(2)-O(3) | 76.3(3) |
| O(8)-W(1)-O(3) | 177.0(4) | O(1)-W(2)-O(4)#1 | 152.1(4) |
| O(8)-W(1)-O(7) | 100.5(4) | O(1)-W(2)-O(7)#1 | 87.4(4) |
| O(8)-W(1)-O(9) | 105.1(4) | O(1)-W(2)-O(9) | 87.7(4) |
| O(8)-W(1)-W(2) | 136.8(4) | O(1)-W(2)-W(1) | 82.0(3) |
| O(7)-Cu(1)-N(3) | 133.8(4) | O(7)-Cu(1)-N(1) | 114.3(4) |
| N(2)-Cu(1)-O(7) | 91.8(4) | N(4)-Cu(1)-O(9) | 94.6(4) |
| N(2)-Cu(1)-N(1) | 81.3(5) | N(4)-Cu(1)-N(2) | 173.6(5) |
| N(2)-Cu(1)-N(3) | 93.7(5) | N(4)-Cu(1)-N(3) | 81.9(5) |

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,-y+1/2,-z+1.