Electronic Supplementary Information

$[Co_xCu_{1-x}(DDOP)(OH_2)(NO_3)](NO_3)$: Hydrogen Bond-Driven Distortion of Cobalt(II) by Solid Solution ‘Network Mismatch’

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1. ORTEP presentations of $[Co_{0.1}Cu_{0.9}(DDOP)(NO_3)(H_2O)](NO_3)$ (5) and $[Co_{0.7}Cu_{0.3}(DDOP)(NO_3)(H_2O)](NO_3)$ (6)

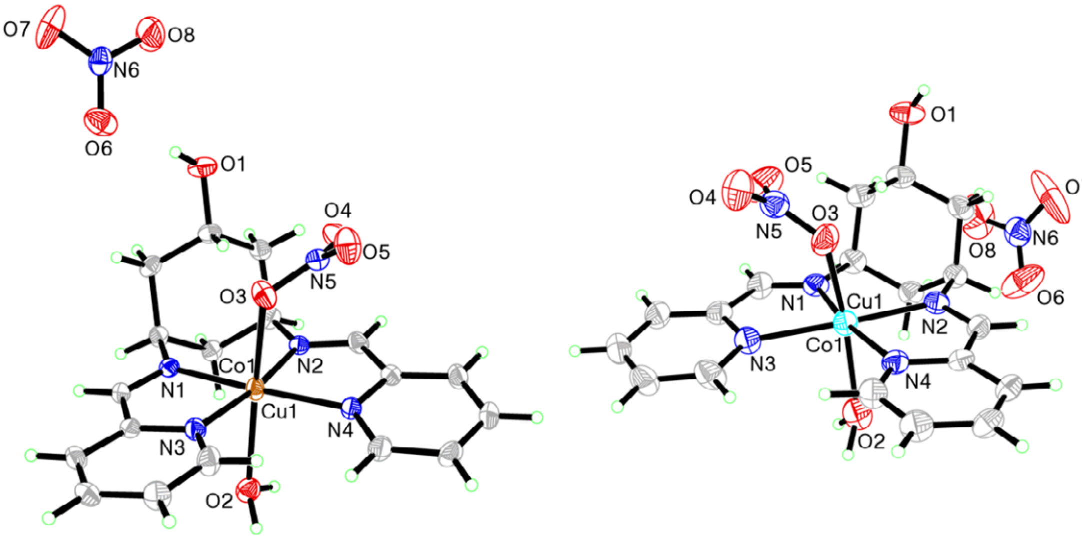

Figure S1. Crystal structures of compounds **5** (left) and **6** (right). ADP ellipsoids are drawn at 50% probability level. C atoms are grey; N, blue; O, red; Co, brown; Cu; cyan; H atoms are white spheres of arbitrary radius. As seen in these plots the two structures show no significant signs of positional disorder in the complex cations.

2. Estimation of Minimum Cobalt(II) Coordination Sphere Distortion in $[Co_{0.4}Cu_{0.6}(DDOP)(NO_3)(H_2O)](NO_3)$ (4)

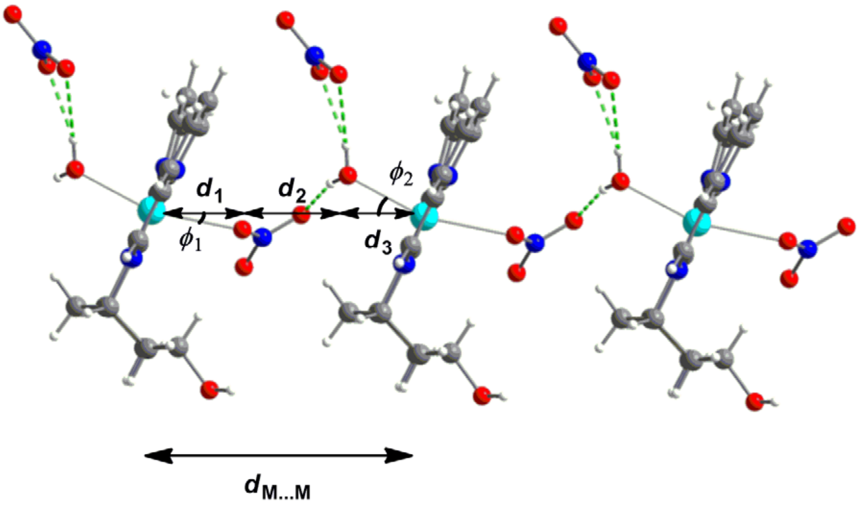

Figure S2. Analysis of the network structure in **4** allowing estimation of cobalt coordination sphere distortion.

The networks of **1** to **4** can be defined by four distances and two angles (Figure S2):

$d_{M\cdots M}$ = the metal-metal distance

$d_1 = \cos(\phi_1) \times R_{M\text{-}ONO2}$

$d_2 = d_{M\cdots M} - d_1 - d_3$: this can be seen as a hydrogen-bond network determined distance retained by each network

$d_3 = \cos(\phi_2) \times R_{M\text{-}OH2}$

ϕ_1 and ϕ_2 are the angles between the M···M axis and their respective M–O coordinate bonds.

Due to the lack of apparent disorder in the structure of **4**, and the small thermal ellipsoids, we consider that the actual geometries of Co and Cu in **4** must be very close to the crystallographically observed average: it is impossible to calculate any other scenario with a high level of confidence. However, here we estimate Co bond lengths for an extreme case where copper retains the bond lengths observed in compound **2**, while $d_{M\cdots M}$, d_2, ϕ_1 and ϕ_2 are exactly those measured in **4**. This provides an estimate of the minimum possible distortion to the cobalt(II) coordination sphere. So, in this case:

$d_{M\cdots M} = 7.357$ Å; $d_2 = 2.951$ Å; $\phi_1 = 11.77°$ and $\phi_2 = 28.54°$: these values are taken from structure **4** and assumed to be constant.

For copper: $\boldsymbol{R}_{\mathbf{Cu\text{-}ONO2}} = 2.515$ Å, so $\boldsymbol{d}_{\mathbf{1Cu}} = 2.462$ Å; $\boldsymbol{R}_{\mathbf{Cu\text{-}OH2}} = 2.364$ Å, so $\boldsymbol{d}_{\mathbf{3Cu}} = 2.077$ Å

For cobalt: $\boldsymbol{d}_{\mathbf{1Co}} = \boldsymbol{d}_{\mathbf{M\cdots M}} - \boldsymbol{d}_{\mathbf{2}} - \boldsymbol{d}_{\mathbf{3Cu}} = 2.329$ Å, so: $\boldsymbol{R}_{\mathbf{Co\text{-}ONO2}} = 2.379$ Å

$\boldsymbol{d}_{\mathbf{3Co}} = \boldsymbol{d}_{\mathbf{M\cdots M}} - \boldsymbol{d}_{\mathbf{2}} - \boldsymbol{d}_{\mathbf{1Cu}} = 1.944$ Å, so: $\boldsymbol{R}_{\mathbf{Co\text{-}ONO2}} = 2.213$ Å

This corresponds to estimated minimum axial elongations versus the pure cobalt compound **1** of around 0.23 Å to the nitrato ligand and 0.075 Å to the aqua ligand. These are substantial. Of course, keeping $\boldsymbol{d}_{\mathbf{M\cdots M}}$ to the value observed in **4**, and using $\boldsymbol{d}_{\mathbf{2}}$, ϕ_1 and ϕ_2 values from **1** or **2** will give different estimates. However, these are largely similar to the above.