# Electronic supplementary Information (ESI)

# Assembly of dinuclear copper(II) secondary building units into polymeric complexes: crystal structures and magnetic properties

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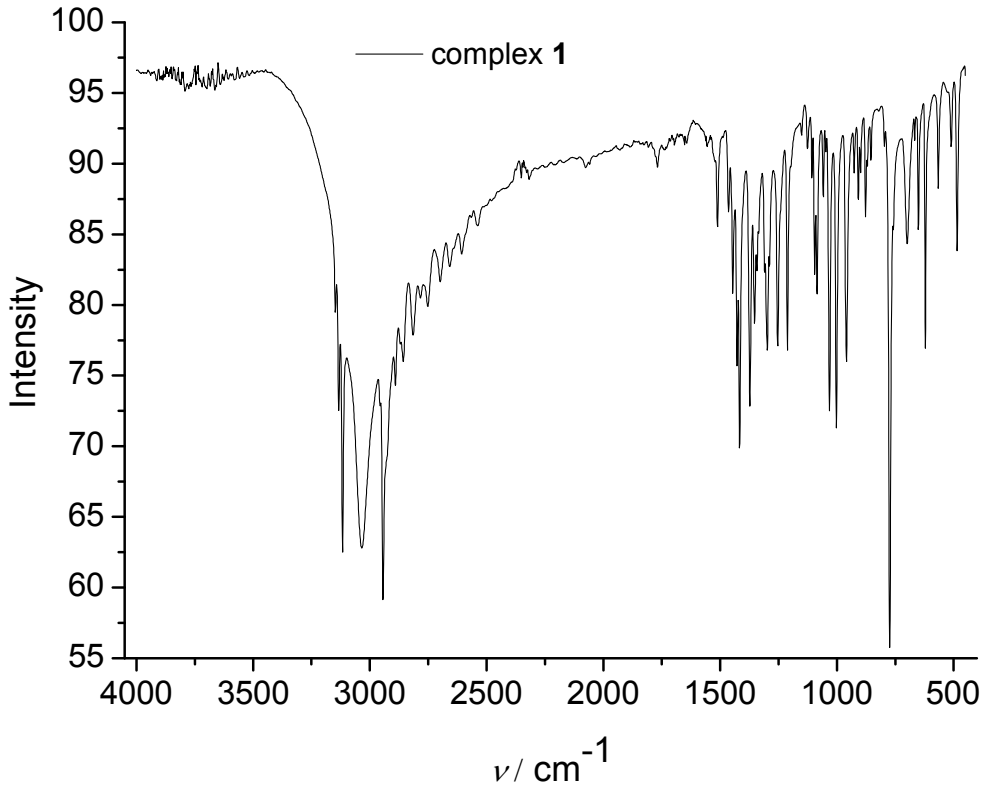


**Figure S1**. IR spectrum for complex **1**

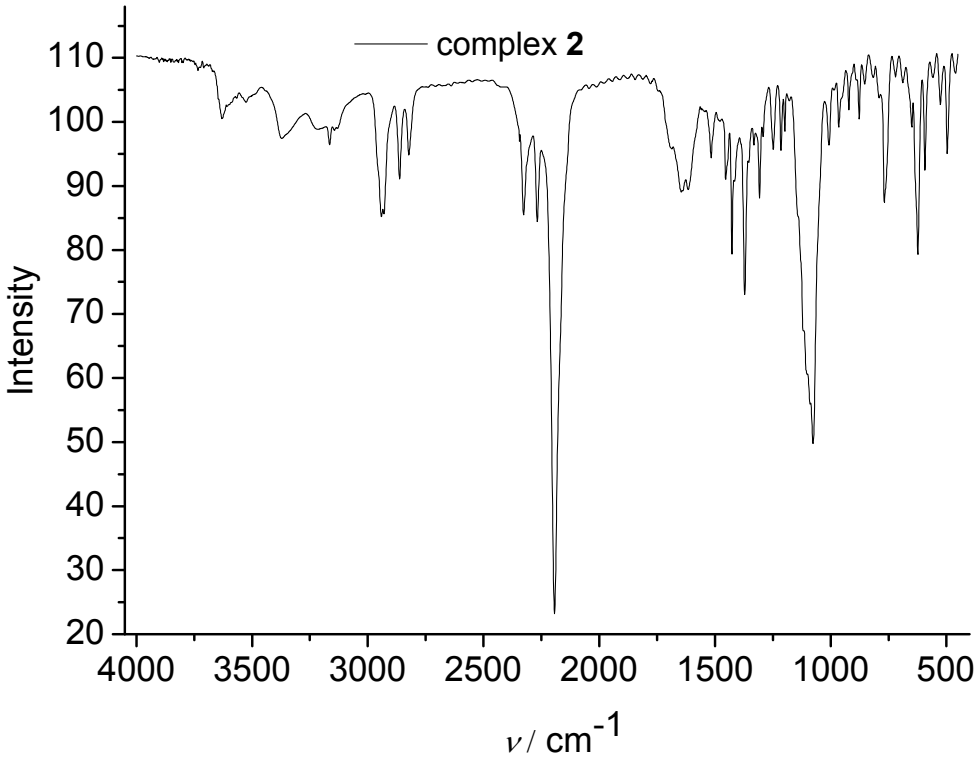


**Figure S2**. IR spectrum for complex **2**

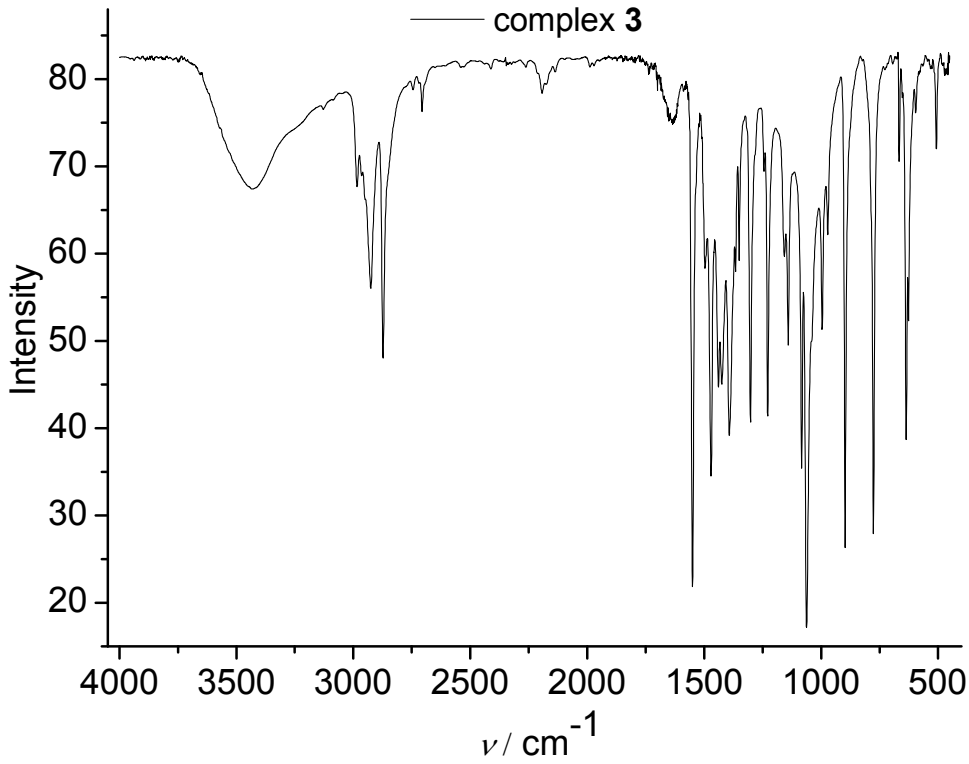


**Figure S3**. IR spectrum for complex **3**

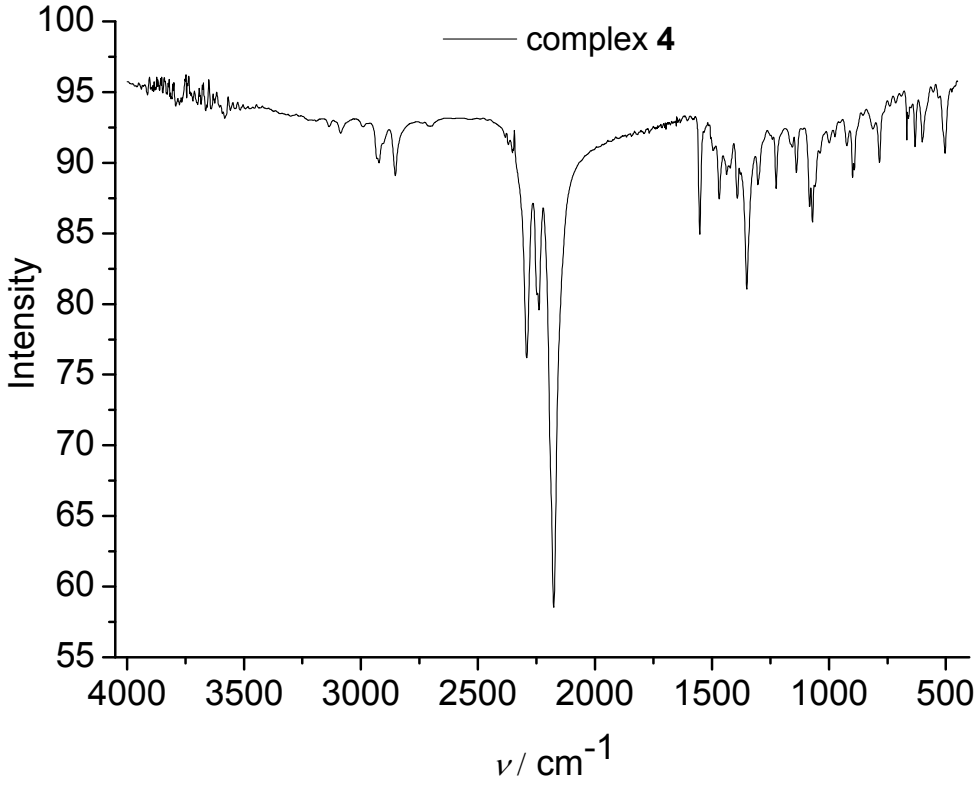


**Figure S4**. IR spectrum for complex **4**

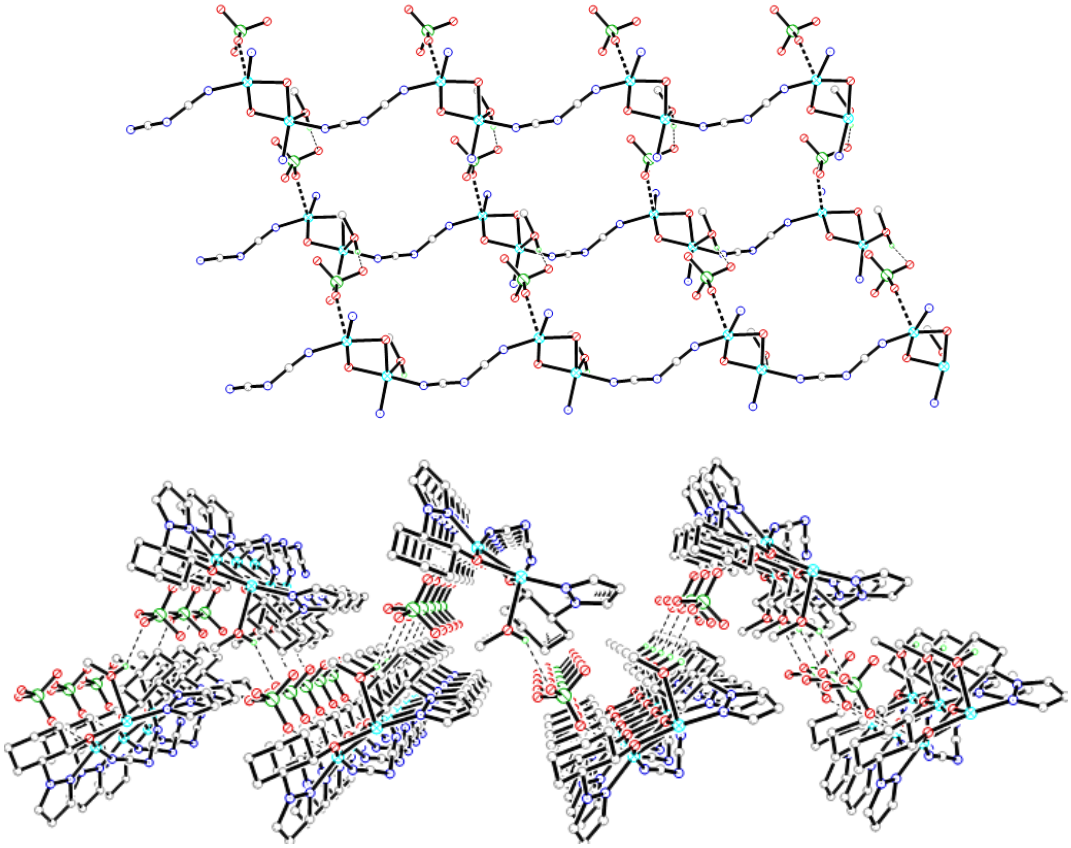

**Figure S5**. Hydrogen-bonded 2D structure for complex **2**. Top: view along the *b* axis. Bottom: view along the *a* axis.

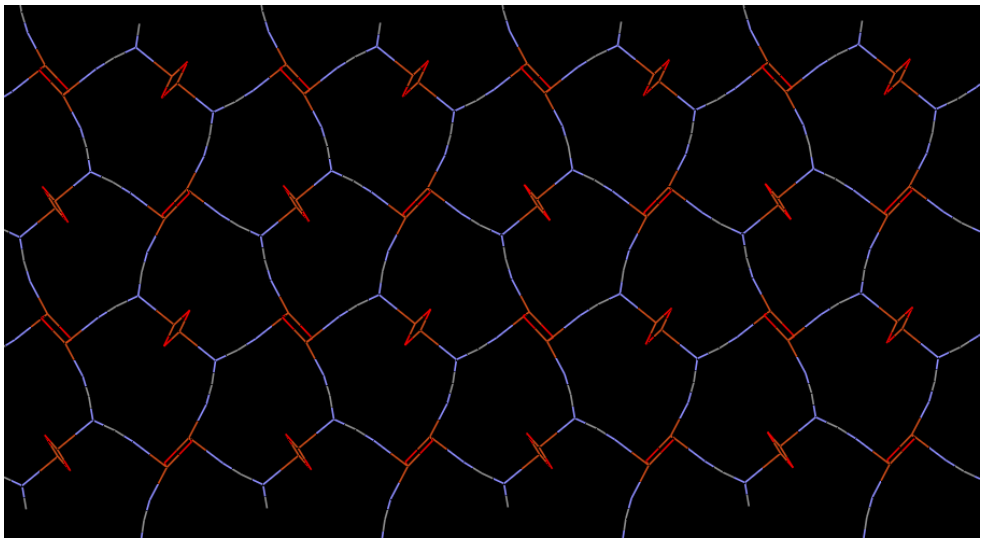

Fig. S6. 2D layered structure of complex **4**. Only $Cu_2O_2$ units and bridging dicyanamides are shown.

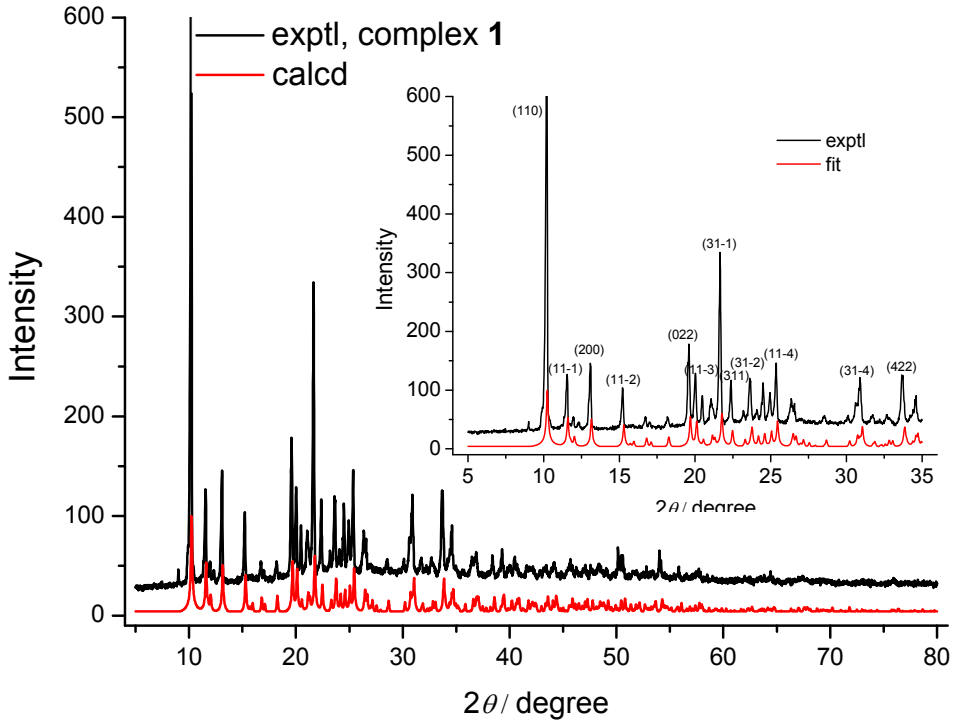


**Figure S7**. Powder XRD and calculated XRD from single crystal data for complex **1**. Inset: Indexing of the powder XRD for complex **1**.

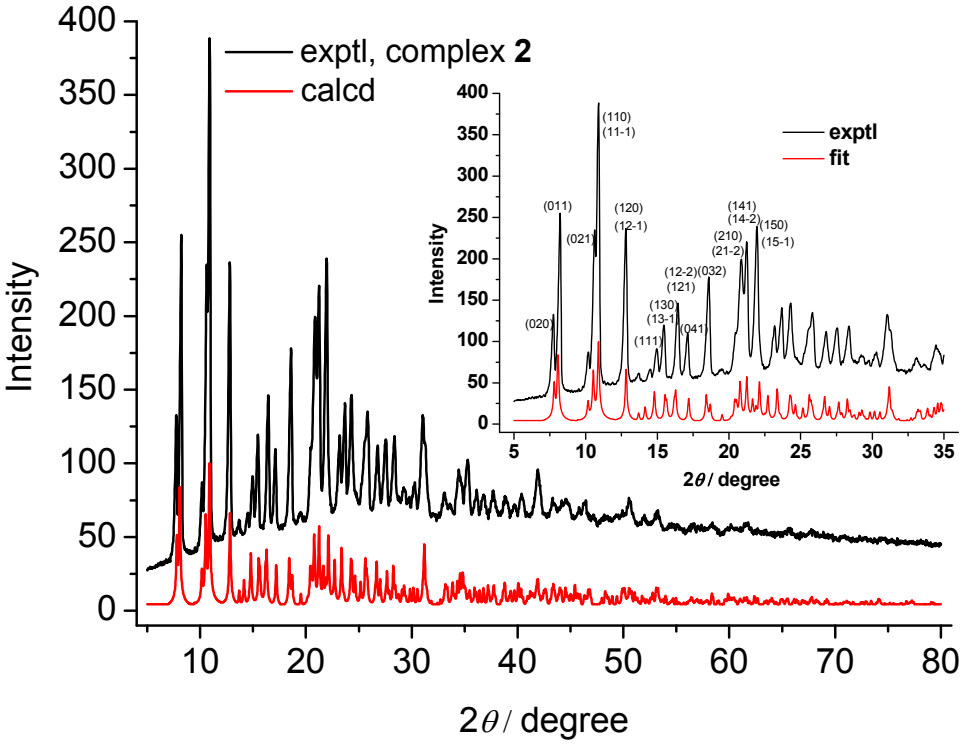


**Figure S8**. Powder XRD and calculated XRD from single crystal data for complex **2**. Inset: Indexing of powder XRD for complex **2**.

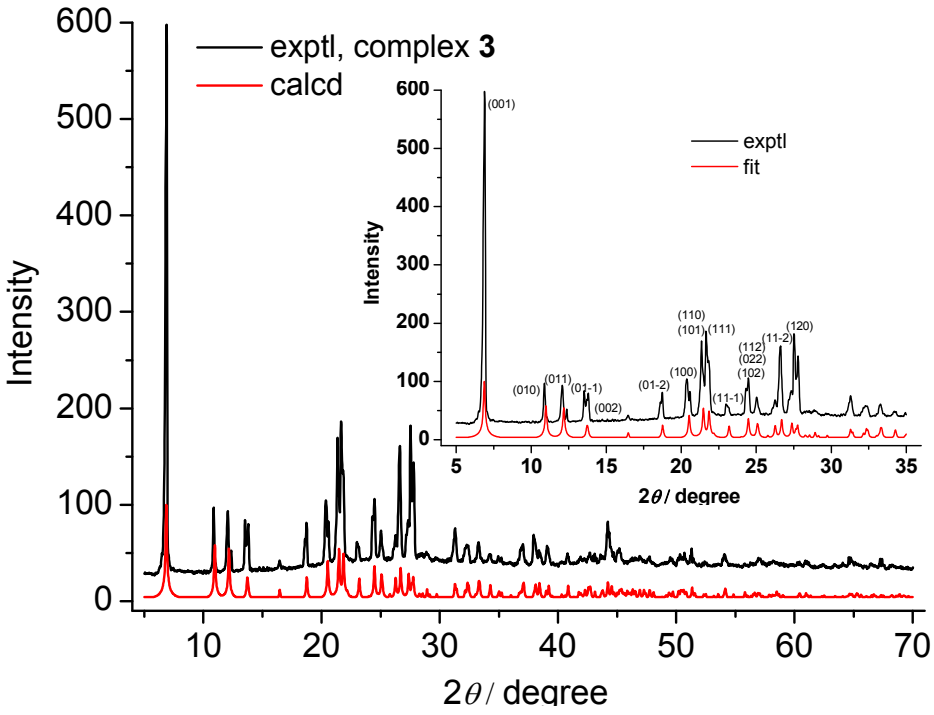


**Figure S9**. Powder XRD and calculated XRD from single crystal data for complex **3**. Inset: Indexing of powder XRD for complex **3**.

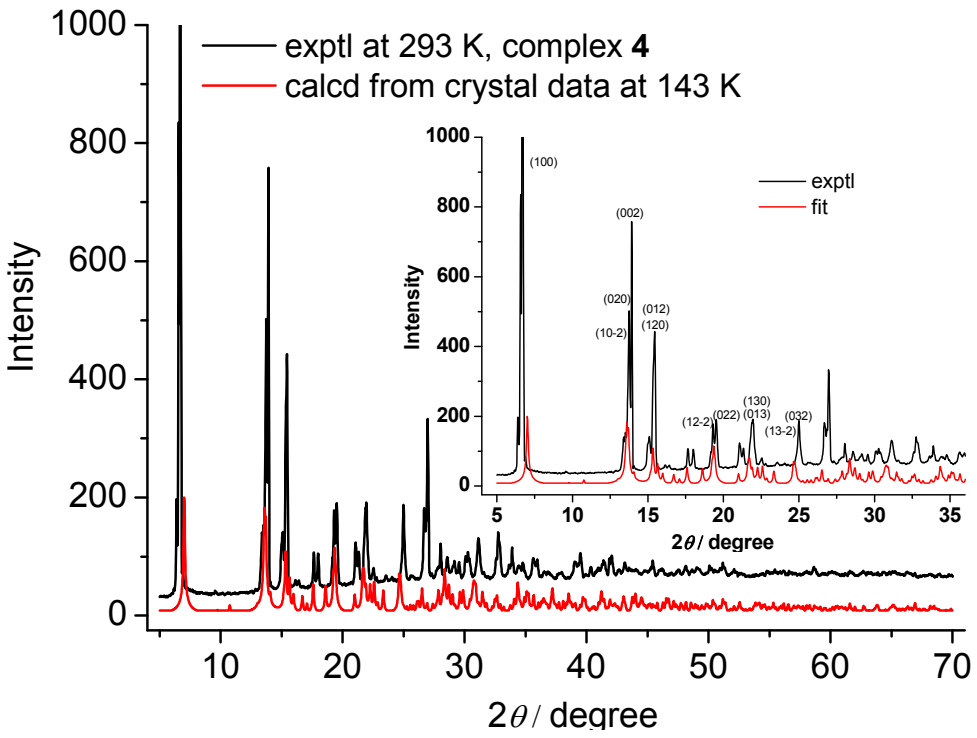


**Figure S10**. Powder XRD at 293 K and calculated XRD from single crystal data at 143 K for complex **4**. Inset: Indexing of powder XRD for complex **4**.

**Table S1.** Comparison of cell parameters derived from single-crystal XRD and powder XRD data[a]

| Single-crystal /powder XRD | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| *a*, Å | 13.478(4) / 13.547(4) | 9.2753(6) / 9.26(1) | 4.4013(9) / 4.424(7) | 13.095(3) / 13.7(2) |
| *b*, Å | 11.259(4) / 11.323(8) | 22.626(2) / 22.87(3) | 8.266(2) / 8.29(3) | 13.001(3) / 12.81(4) |
| *c*, Å | 15.046(4) / 15.081(6) | 13.334(1) / 13.03(3) | 12.976(3) / 13.00(5) | 13.439(3) / 13.36(5) |
| *α*, deg | 90 / 90 | 90 / 90 | 82.02(3) / 82.1(3) | 90 / 90 |
| *β*, deg | 93.77(3) / 93.97(3) | 110.287(2) / 110.6(1) | 87.00(3) / 87.0(2) | 106.17(3) / 106.7(7) |
| *γ*, deg | 90 / 90 | 90 / 90 | 79.24(3) / 79.2(2) | 90 / 90 |
| *V*, Å$^3$ | 2278(1) / 2308(1) | 2624.7(3) / 2583(5) | 459.1(2) / 464(2) | 2197.3(8) / 2250(30) |

[a] Data obtained by using the UnitCell software.

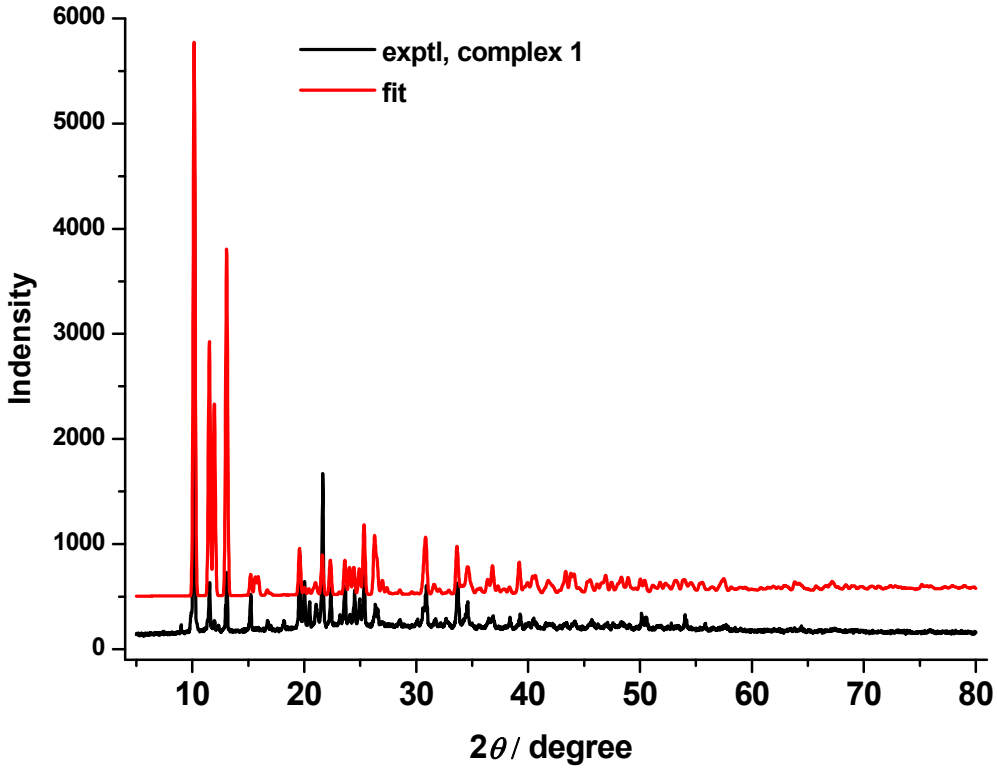


**Figure S11**. Powder XRD and Rietveld fit for complex **1**.

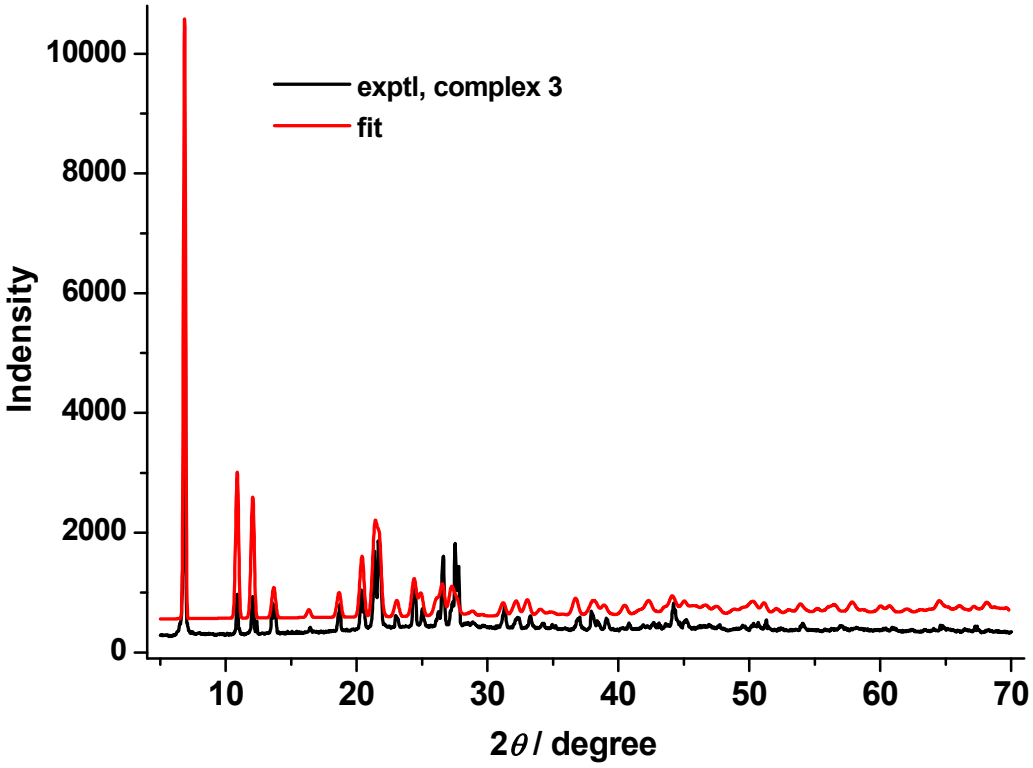


**Figure S12**. powder XRD and Rietveld fit for complex **3**.

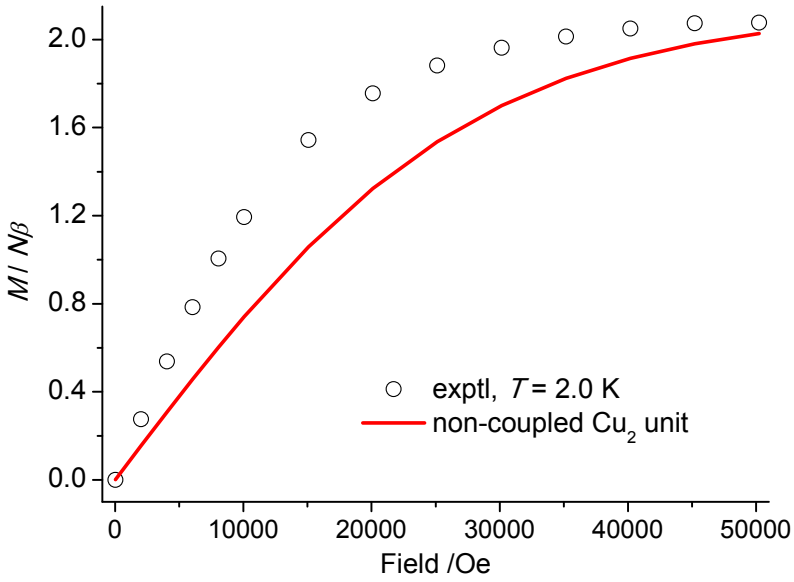


**Fig. S13**. Field dependence of magnetization for complex **1** (per $Cu_2$).The solid line represents the Brillouin function for two isolated Cu(II) ions.