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Electronic Supplementary Information

End-on cyanate or end-to-end thiocyanate bridged dinuclear copper(II) complexes with a tridentate Schiff base blocking ligand: Synthesis, structure and magnetic studies

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Experimental Section

All chemicals were of reagent grade and used as purchased from Sigma-Aldrich without further purification.

Physical Measurements

Elemental analysis (carbon, hydrogen, and nitrogen) was carried out using a Perkin-Elmer 2400 II elemental analyzer. IR spectra in KBr (4000-500 cm^{-1}) were recorded using a Parkin Elmer RXI FTIR spectrophotometer. Electronic spectra in acetonitrile (1000–200 nm) were recorded in a Hitachi U-3501 spectrophotometer. The XRD data of the powdered sample were collected on a Bruker D8 Advance X-ray diffractometer using with Cu K_{α} radiation (λ= 1.548 Å) generated at 40 kV and 40 mA. The PXRD spectra were recorded in a 2θ range of 5–50° using 1-D Lynxeye detector at ambient conditions. Electro-spray ionization mass spectra were recorded with Waters QTOF Micro YA263. A Quantum Design MPMSXL SQUID (Superconducting Quantum Interference Device) magnetometer was used to measure the variable-temperature magnetic properties. The temperature range was 2–300 K under an applied magnetic field of 5000 Oe. The signal of the sample holder was taken into account to correct the measured data, as well as the molar diamagnetic corrections for the compound, which were calculated on the basis of Pascal's constants.[1-2] Fits were performed using the program *julX*.

X-ray crystallography

Single crystals of both complexes were used for data collection using a Bruker D8 QUEST area detector diffractometer equipped with graphite-monochromated Mo K_{α} radiation (λ = 0.71073 Å) at 100 K. The molecular structures were solved by direct method and refined by full-matrix least squares on F^2 using SHELXL-2016.[3] X-ray intensity data were measured. The frames were integrated with the Bruker SAINT Software package using a wide-frame algorithm. Non hydrogen atoms were refined anisotropically. Hydrogen atoms attached to oxygen and nitrogen atoms were located by difference Fourier maps and were kept at fixed positions. Other hydrogen atoms were placed in their geometrically idealised positions and constrained to ride on their parent atoms. Numerical and/or multi-scan absorption corrections were applied to the data using the program SADABS.[4]

Hirshfeld surfaces

Hirshfeld surface analysis was explored to evaluate the structural flexibility and magnitude of each interchain interaction in both complexes. Hirshfeld surfaces[5-7] and associated 2D-fingerprint[8-10] plots were obtained using Crystal Explorer 3.[11] This analysis is useful for the evaluation of closest intermolecular atomic contacts, even in complex crystal structures.[12]

X-ray powder diffraction pattern

The experimental powder x-ray diffraction patterns of the bulk products agree well with the simulated XRD patterns generated from cif. This indicates purity of the bulk samples. Fig. S1 and Fig. S2 show the experimental and simulated XRD patterns for complexes **1** and **2,** respectively.

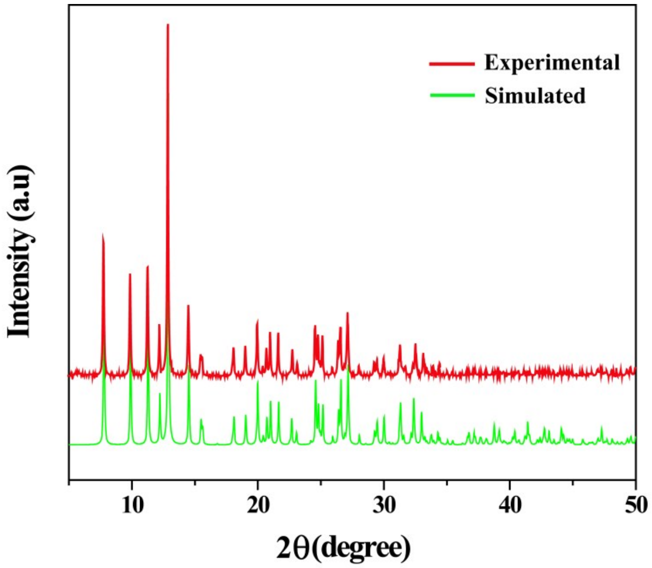

Fig. S1: Experimental and simulated powder XRD patterns of the complex **1** confirming the purity of bulk material.

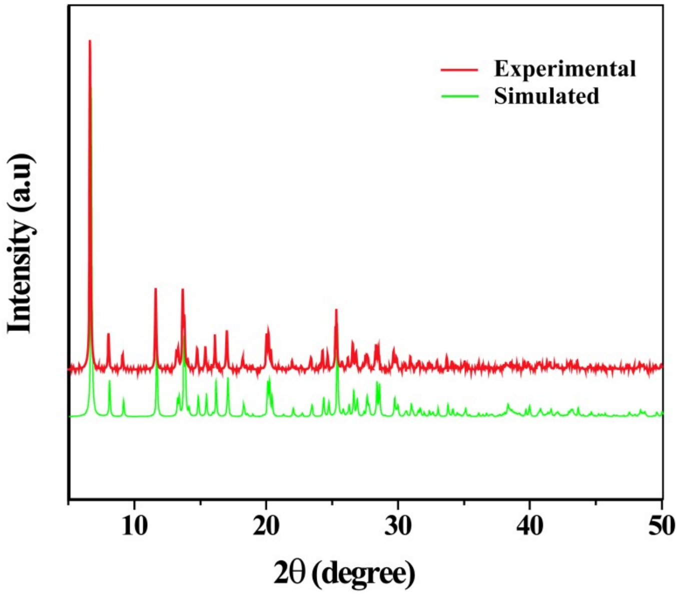

Fig. S2: Experimental and simulated powder XRD patterns of the complex **2** confirming the purity of bulk material.

Hirshfeld surface analysis

The Hirshfeld surfaces of both complexes, mapped over d_{norm}, shape index and curvedness, are illustrated in Fig. S3. The intermolecular interactions appear as distinct spikes in the 2D fingerprint plot (Fig. S4). we can decompose the fingerprint plot to highlight separate interactions.[13] The common features of Hirshfeld surfaces is the widespread presence of several red spots that are mostly recognized as C···H, O···H and N···H contacts. The proportions of C···H/H···C, interactions comprise 21.3 and 15.9% of the total Hirshfeld surfaces, respectively for each molecule of for **1** and **2**, whereas O···H/H···O interaction comprises of 19.1 and 11.9% to the total Hirshfeld surfaces, respectively for **1** and **2**.

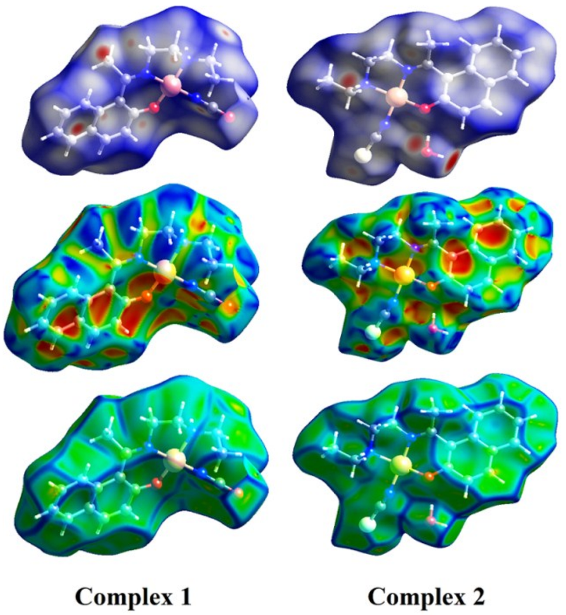

Fig. S3: Hirshfeld surfaces mapped with d_{norm} (top), shape index (middle), curvedness (bottom) for complexes **1** and **2**.

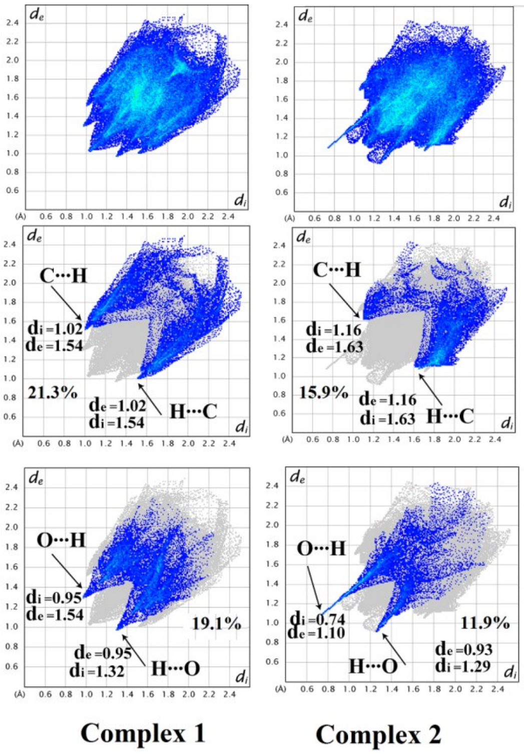

Fig. S4: 2D fingerprint plots: Full (top); O···H/H···O (middle) N···H/H···N (bottom) interactions contributed to the total Hirshfeld surface area of complexes **1** and **2**.

References

1. P. Pascal, *Ann. Phys. Chim.* 1910, **19**, 5*; Ann. Phys. Chim.* 1912, **25**, 289*; Ann. Phys. Chim.* 1913, **28**, 218.

2. G. A. Bain, J. F. Berry, *J. Chem. Educ*. 2008, **85**, 532-536.

3. G. M. Sheldrick, *Acta crystallographica. Section C, Structural chemistry* 2015, **71**, 3–8.

4. SADABS. Bruker AXS area detector scaling and absorption correction, Bruker AXS Inc., Madison, Wisconsin, USA, **2014**.

5. M. A. Spackman and D. Jayatilaka, *CrystEngComm,* 2009, **11**, 19-32.

6. F. L. Hirshfeld, *Theor. Chim. Acta,* 1977, **44**, 129-138.

7. H. F. Clausen, M. S. Chevallier, M. A. Spackman and B. B. Iversen, *New J. Chem*., 2010, **34**, 193-199.

8. A. L. Rohl, M. Moret, W. Kaminsky, K. Claborn, J. J. McKinnon and B. Kahr, *Cryst. Growth Des*., 2008, **8**, 4517-4525.

9. A. Parkin, G. Barr, W. Dong, C. J. Gilmore, D. Jayatilaka, J. J. McKinnon, M. A. Spackman and C. C. Wilson, *CrystEngComm* 2007, **9**, 648-652.

10. M. A. Spackman and J. J. McKinnon, *CrystEngComm* 2002, **4**, 378-392.

11. S. K. Wolff, D. J. Grimwood, J. J. McKinnon, D. Jayatilaka and M. A. Spackman, Crystal Explorer 2.0; University of Western Australia: Perth, Australia, 2007. http://hirshfeldsurfacenet.blogspot.com/.

12. M. A. Spackman, and D. Jayatilaka, *CrystEngComm* 2009, **11**, 19−32.

13. M.A. Spackman and P.G. Byrom, *Chem. Phys. Lett.* 1997, **267**, 215–220.