Systematic Screening for *k* Type Phase Transitions – General Approach and Positive Example for a Binuclear Cu(II) Paddlewheel Structure – Supporting Information

Robert Strothmann, Steven van Terwingen, Irmgard Kalf, and Ulli Englert[*]

S1 X-ray crystallography

S1.1 Structure determination

Intensity data were collected with a Bruker D8 goniometer equipped with an APEX CCD area detector and an Incoatec microsource (Mo-K_α radiation, $\lambda = 0.71073\,\text{Å}$, multilayer optics). Temperature was maintained by using an Oxford Cryostream 700 instrument, Oxfordshire, UK. Data was integrated with SAINT[1] and corrected for absorption by multi-scan methods.[2] The structures were solved by intrinsic phasing[3] and refined by full matrix least squares procedures against F^2, as implemented in SHELXL-18.[3] For all temperatures, hydrogen atoms located on oxygen atoms were refined freely with a distant restraint amounting to $0.85\,\text{Å}$ for $T = 100\,\text{K}$. For all other temperatures, hydrogens located on oxygen atoms were constrained to their positions from the difference Fourier synthesis. Hydrogen atoms located on carbons were treated as riding with $C-H = 0.98\,\text{Å}$ for CH_3, $C-H = 0.95\,\text{Å}$ for aryl-CH and $C-H = 0.99\,\text{Å}$ for alkyl-CH_2 groups for $100\,\text{K}$ and $C-H = 0.96\,\text{Å}$ for CH_3, $C-H = 0.93\,\text{Å}$ for aryl-CH and $C-H = 0.97\,\text{Å}$ for alkyl-CH_2 groups for $300\,\text{K}$. All temperatures used the standard values for their specific temperature defined distances in SHELXL-18 and can be found in the SHELX manual.[3] They were assigned isotropic displacement parameters constrained to $U_{\text{iso}}(\text{H}) = 1.5\,U_{\text{eq}}(\text{C(methyl)})$ or $U_{\text{iso}}(\text{H}) = 1.2\,U_{\text{eq}}(\text{C(aryl, methylene)}, \text{O(hydroxy)})$ otherwise. For all split atom sites the ethanol atoms' ADPs of the major component were treated with a rigid bond restraint. Additionally, distance restraints with $d(\text{C}-\text{O}) = 1.4\,\text{Å}$ and $d(\text{C}-\text{C}) = 1.5\,\text{Å}$ were applied for all non-hydrogen atoms in the disordered ethanol moieties. The carbon atoms of a lower occupancy than 0.5 were refined isotropically with $U_{\text{iso}}(\text{C(minor)}) = 1.3\,U_{\text{iso}}(\text{C(major)})$. Furthermore, a similarity restraint was applied to all carbon atoms of the disordered atom sites. Additional information can be found in the corresponding CIF files.

S1.2 Crystal parameters and convergence results

Table S1 Crystal parameters for the temperature-dependent measurements.

Crystal	T / K	Size / mm^3
1*	100(2), 210(2), 220(2), 224(2), 228(2), 232(2), 236(2), 240(2), 250(2)	$0.15 \times 0.05 \times 0.03$
2	200(2), 220(2), 250(2), 300(2)	$0.20 \times 0.05 \times 0.05$
3	210(2), 230(2), 240(2)	$0.12 \times 0.03 \times 0.03$

* For crystal 1 only one full measurement was accomplished at $100(2)\,\text{K}$. All other measurements of this crystal were reduced data collections with focus on determining the pseudo symmetry from strong reflections.

Table S2 Refinement results for the specific full measurements for $C_{32}H_{28}Cu_2I_4O_{10}$ (**1**) in the triclinic space group $P\bar{1}$. Columns marked in <mark>yellow</mark> are solved in the high temperature phase.

Temperature / K	100(2)	200(2)	210(2)	220(2)	230(2)	240(2)	250(2)	300(2)
crystal No.	1	2	3	2	3	3	2	2
a / Å	12.2327(7)	12.2984(6)	12.3144(9)	12.3110(7)	12.3254(9)	6.5823(17)	6.5859(3)	6.608(2)
b / Å	13.0214(7)	13.0766(7)	13.0777(9)	13.0867(7)	13.0852(9)	11.601(3)	11.5949(5)	11.633(3)
c / Å	13.0009(7)	13.0960(7)	13.1092(9)	13.1261(7)	13.1410(9)	13.001(3)	13.0118(6)	13.025(5)
α / °	74.4145(18)	74.6019(8)	74.5741(12)	74.6390(9)	74.6086(12)	91.653(4)	91.610(2)	91.803(8)
β / °	68.2545(17)	67.9382(8)	68.0058(11)	67.9332(8)	68.0040(12)	103.841(4)	103.887(2)	104.018(6)
γ / °	87.4839(18)	87.6692(8)	87.7900(12)	87.7934(9)	87.9267(12)	99.765(5)	99.737(2)	99.843(17)
V / Å^3	1849.19(18)	1877.72(17)	1882.6(2)	1885.41(18)	1889.9(2)	947.5(4)	948.23(7)	954.3(5)
Z	2	2	2	2	2	1	1	1
D_{calc} / g cm^{-3}	2.168	2.135	2.130	2.126	2.121	2.116	2.114	2.101
μ / mm^{-1}	4.541	4.472	4.461	4.454	4.444	4.432	4.428	4.400
$\theta_{min}/\theta_{max}$ / °	1.63/36.46	1.74/28.52	1.74/28.51	1.74/28.53	1.74/28.52	2.32/28.55	2.32/28.56	2.31/28.42
total/unique refl.	70897/17730	26788/9483	26937/9505	26950/9538	27044/9551	13532/4807	13528/4822	13485/4784
observed refl.	10374	5719	3787	5066	3495	2584	3648	3366
No. of parameters	441	442	442	449	437	229	229	229
R_{int}	0.0689	0.0381	0.0912	0.0420	0.0924	0.0699	0.0356	0.0364
$R(I > 2\sigma(I))$	0.0480	0.0396	0.0534	0.0431	0.0564	0.0464	0.0383	0.0395
wR_2	0.1178	0.1048	0.1232	0.1235	0.1114	0.0982	0.0916	0.0996
S	1.025	1.011	0.914	1.001	1.017	0.929	1.013	1.044
ρ_{min}/ρ_{min} / eÅ^{-3}	−1.404/1.657	−0.626/1.171	−0.769/1.030	−0.564/1.303	−0.795/0.790	−0.751/0.958	−0.680/0.983	−0.684/1.052
CCDC #	2039840	2039835	2039841	2039836	2039837	2039838	2039842	2039839

S1.3 Miscellaneous
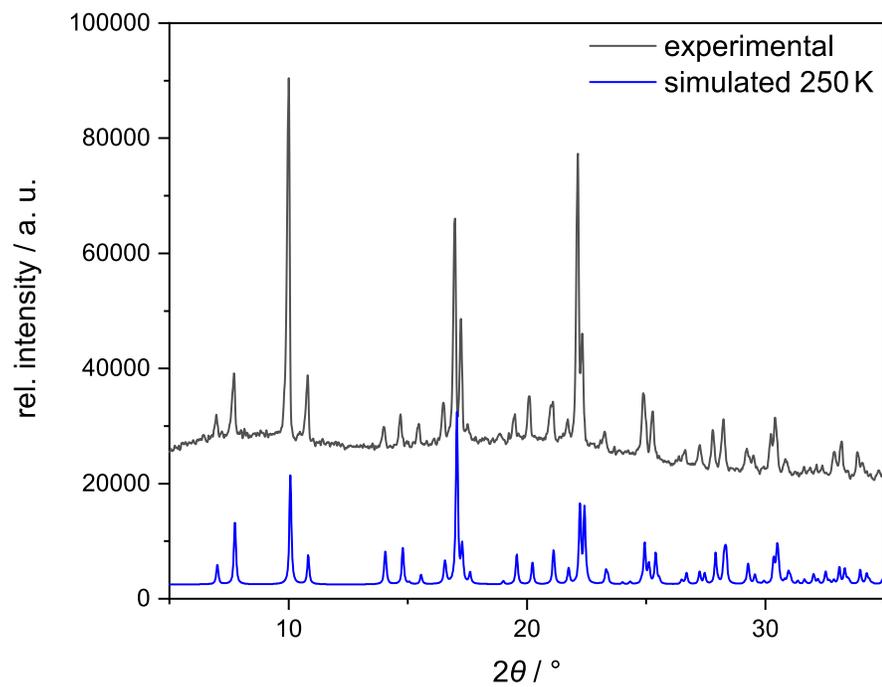
Figure S1 Experimental powder diffraction pattern of **1** (room temperature) and simulated from the 250 K measurement displayed from $2\theta = 5°$ to $35°$.
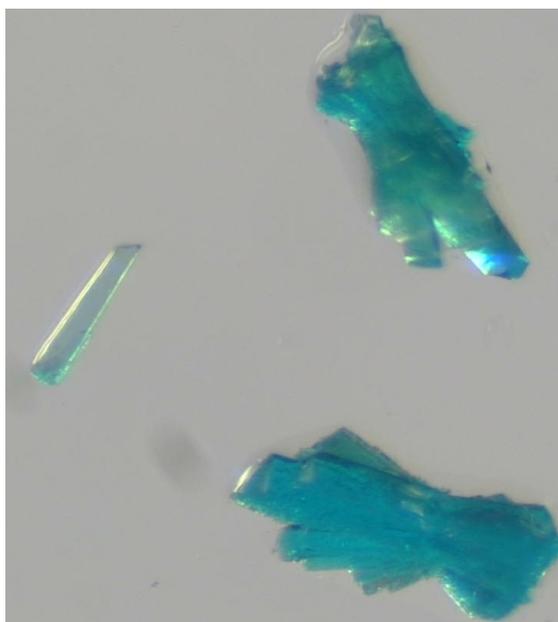
Figure S2 Typical single crystal (left) and two crystal clusters of **1** at two angles, in which the dichroistic behavior from green to blue is depicted.

Table S3 Torsion angles describing the twist of the two Cu square pyramidal coordination spheres around the Cu⋯Cu line.

T / K	100	200	250
$\angle$(O–Cu⋯Cu–O)	16.7(3)	13.58(15)	1.16(14)
	17.2(2)	14.22(12)	1.16(14)
	15.5(2)	12.15(12)	1.16(16)
	15.5(2)	12.15(12)	1.16(16)

S2 Screening results

S2.1 Reciprocal Space

S2.1.1 Walk-through reciprocal space analysis

The screening was accomplished within five steps using pre-implemented functions of PLATON,[4] bash as well as Python[5] scripting:

1. The user needs to define a set of data based on the ConQuest CSD application with query terms.[6] Examples for search attributes are quality of underlying data, year of publication, the journal published in or different elements in the structure. The `.cif` files obtained in this step are saved in one folder.

2. Bash scripting can be used to automatically run the following steps for all `.cif` files in the previous folder. Therefore one needs to assign the folder path to the script as an input value and the following tasks looping over all `.cif` files in the folder.

3. The first step in the loop is using PLATON commands in the console to recalculate the *hkl* and their respective intensity values from the `.cif` file and save it into the same folder. PLATON can be run with the `-o` option without an interface for this step. This is the most expensive step regarding computational time.

4. In the next step the `.hkl` file is renamed and used together with the generated `.res` file to calculate a `.lis` file containing information about the systematic absences. All non-essential temporary files will be deleted afterwards resulting in a folder containing only `.lis` files.

5. The last part is the analysis of the `.lis` files using Python. The relevant information are gathered by looping over all files. Systematic absences are represented as height of the value as well as reflection class. A simple scatter plot of the name and height of the value is one possible way to present the results. A hit list with all relevant information can be saved for further usage.

S2.1.2 Reciprocal space analysis results for hit rate of different journals

Table S4 Reciprocal space analysis for different subsets based on academic journals (Data requested September 2019).

Journal	Period of time	# Structures	Hitrate
Acta Crystallogr. B	1983-2012	2589	4.5 %
Nature Chemistry	2001–2014	454	3.5 %
Acta Crystallogr. E	2001–2014	27651	3.1 %
Angew. Chem. Int. Ed.	1960–2017	12927	2.6 %
Z. Kristallogr. – NCS	1997–2017	2985	3.9 %
Z. Kristallogr. – Cryst. Mater.	2001–2014	1770	4.3 %
Crystals	2011–2017	200	1.0 %
CrystEngComm	1998–2013	135	1.4 %

S2.2 Real Space

S2.2.1 Walk-through real space analysis

Since this part is more work in progress only conceptual steps will be mentioned here. All steps are performed in Python using a folder of `.cif` files and a hit-rate list created in the reciprocal space analysis.

1. The first step is the data input and assigning of all variables as well as importing all additional functions. The coordinates, symmetry equivalent positions and unit cell axis and angles are based on the `.cif` files, the pseudo translations and associated pseudo reflection conditions are based on the hit rate list file.

2. Fractional coordinates are checked and, if necessary, replaced by translationally equivalent values $0 < x < 1$. The `.cif` files may contain residues belonging to several unit cells and do not necessarily contain connected sets. This is checked but still requires manual intervention.

3. With the use of covalent radii[7] the asymmetric unit can be split into different fragments.

4. Based on the structure modified as above, the script can create a unit cell with the aid of the symmetry equivalent positions. Furthermore, additional 26 unit cells are created that are directly surrounding the first one by just translating in all possible directions with ±1. The 26 unit cells surrounding the central cell with coordinates between 0 and 1 are required when constituents belong to more than one cell. For the overlap calculations, fractional coordinates are converted to cartesian coordinates with the help of a python script.

5. The best overlapping pairs of unit cells for all fragments are assigned by comparing the mean distance between each original fragment and one obtained by the pseudo translation. Based on that selection a more specific nearest atom to atom pair distance can be computed resulting in the fragment resolved distance criteria.
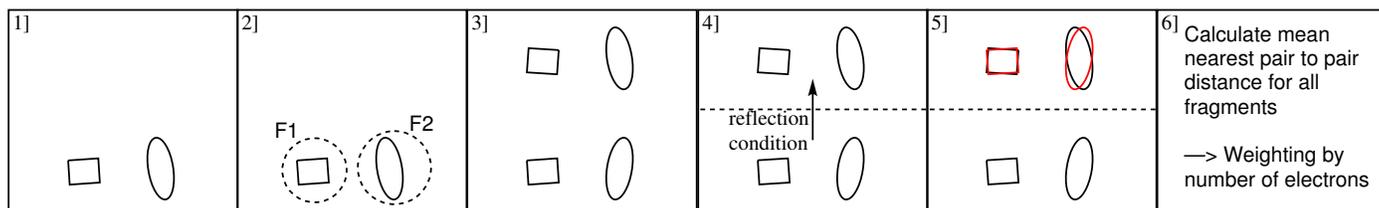
Figure S3 .

Notes and references

[1] Bruker, *SAINT+: Program for Reduction of Data Collected on Bruker CCD Area Detector Diffractometer*, 2009.

[2] Bruker, *SADABS*, 2014.

[3] G. M. Sheldrick, *Acta Crystallogr.*, 2015, **A71**, 3–8.

[4] A. L. Spek, *Acta Crystallogr.*, 2009, **D65**, 148–155.

[5] Python Software Foundation, *Python Language Reference, Version 2.7*, `www.python.org`.

[6] C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallogr.*, 2016, **B72**, 171–179.

[7] B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán and S. Alvarez, *Dalton Trans.*, 2008, **21**, 2832–2838.