

Electronic Supplementary Information (ESI) for

Transition metal coordination complexes of chrysazin

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Contents

S1	Methods	S3
S1.1	Materials and characterisation	S3
S1.2	Synthesis of [Fe(HChrysazinate) ₂ DMF ₂] (FeChrys-1)	S3
S1.3	Synthesis of [Fe ₂ (Chrysazinate) ₃]·DMF·½H ₂ O (FeChrys-2)	S3
S1.4	Synthesis of [Co ₁₂ (Chrysazinate) ₆ (AcO) ₁₂ DMF ₆]·6(DMF) (CoChrys-1)	S3
S1.5	Synthesis of [Co ₃ (Chrysazinate) ₂ (AcO) ₂ DMF ₃ Pyridine] (CoChrys-2)	S3
S1.6	Synthesis of 2[Co ₄ (Chrysazinate) ₄ DMF ₄]·2.35(DMF)·½H ₂ O (CoChrys-3)	S4
S1.7	Synthesis of [Ni ₁₂ (Chrysazinate) ₆ (AcO) ₁₂ DMF ₆]·6(DMF) (NiChrys-1)	S4
S1.8	Synthesis of [Ni ₆ (Chrysazinate) ₄ (AcO) ₄ DMF ₄]·2(DMF) (NiChrys-2)	S4
S1.9	Synthesis of [Cu ₂ (Chrysazinate) ₂] (CuChrys-1)	S4
S1.10	Synthesis of [Cu ₂ (Chrysazinate) ₂]·0.44DMF (CuChrys-2)	S5
S1.11	Synthesis of [Cu ₂ (Chrysazinate) ₂ DMSO ₂] (CuChrys-3)	S5
S1.12	Synthesis of [Cu(HChrysazinate) ₂] (CuChrys-4)	S6
S1.13	Synthesis of [Ni ₂ (1,5-dihydroxy-4,8-dinitroanthraquinone) ₂ DMF ₄] (NiNOChrys-1)	S6
S1.14	High-throughput synthesis	S6
S1.15	Treatment of CuChrys-1 with hydrogen gas	S6
S1.16	Single-crystal X-ray diffraction (SCXRD)	S7
S1.17	Powder X-ray diffraction (PXRD)	S7
S1.18	High-throughput PXRD	S7
S1.19	DC conductivity & AC impedance measurements on CuChrys-1	S7
S1.20	Density functional theory calculations	S8
S2	Supplementary data	S9
S2.1	Single-crystal data summary	S9
S2.2	PXRD	S11

S2.3	IR data	S12
S2.4	Evolution of the reaction between $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$ and chrysazin over time	S13
S2.5	Reaction of CuChrys-1 with H_2	S14
S2.6	Effect of pressure on the band structure of CuChrys-1	S14

S1 Methods

S1.1 Materials and characterisation

Cu(AcO)₂·H₂O (98%+), Ni(AcO)₂·4H₂O (99%+), Co(AcO)₂·4H₂O (97%+) and pyrazine (98%+) were purchased from Acros. Dimethylformamide (lab reagent grade), ethanol (analytical reagent grade), dimethylsulfoxide (analytical reagent grade), and pyridine (lab reagent grade) were purchased from Fisher. Chrysazin (≥98%) and 4,5-dinitrochrysazin (4,5-dihydroxy-1,8-dihydroxyanthraquinone) (96.0%) were purchased from TCI. Fe(AcO)₂ (99.999%) was purchased from Aldrich. Co(OH)₂ (99.9%) was purchased from Alfa Aesar.

Infra-red spectra were collected on a Bruker Tensor-27 ATR spectrometer over the range 600-4000 cm⁻¹.

Elemental analysis was run on an Exeter Analytical Inc. CE-440 Elemental Analyser. Simultaneous differential scanning calorimetry and thermal gravimetric analysis (SDT) was carried out on a TA instruments SDT Q600 under a flow of air of 100 ml/min at a heating rate of 5 °C/minute.

S1.2 Synthesis of [Fe(HChrysazinate)₂DMF₂] (FeChrys-1)

DMF was deaerated by bubbling N₂ for 1 hour. Fe(AcO)₂ (27.8 mg, 0.16 mmol) and chrysazin (52.8 mg, 0.16 mmol) were placed in a 20 ml vial (giving a 1:1 metal:ligand molar ratio). 10 ml of deaerated DMF was added and the vial flushed with N₂ for 30 seconds. The vial was placed in an oven at 90 °C for 17 days. After this time the vial was removed from the oven and allowed to cool to room temperature. At this stage no precipitate had formed, so the vial was left slightly open for the solvent to evaporate. After 14 days, black needle-like crystals were observed in the liquid.

S1.3 Synthesis of [Fe₂(Chrysazinate)₃]·DMF· $\frac{1}{2}$ H₂O (FeChrys-2)

The same procedure as for **FeChrys-1** was followed; however, an older batch of Fe(AcO)₂ was used and had likely partially oxidised. After the reaction was allowed to cool, black lathe crystals were collected.

S1.4 Synthesis of [Co₁₂(Chrysazinate)₆(AcO)₁₂DMF₆]·6(DMF) (CoChrys-1)

Co(AcO)₂·4H₂O (266 mg, 1.07 mmol), chrysazin (176 mg, 0.53 mmol) and DMF (10 ml) were placed in a 20 ml vial (giving a 2:1 metal:ligand molar ratio). The vial was placed in an oven at 90 °C for 7 days. After this time the vial was removed from the oven and allowed to cool to room temperature. The solid was recovered by Büchner filtration and washed on the filter with approximately 10 ml each of DMF and ethanol. Black block-shaped crystals were collected (Yield: 40 mg, 12% with respect to chrysazin). Elemental analysis: Calculated mass % (based on six non-coordinated DMF molecules per molecule of Co₁₂Chrysazin₆(AcO)₁₂DMF₆): C 46.47; H 4.22; N 4.52; Co 19.00; O 25.79. Found mass %: C 45.99; H 4.36; N 4.81. Thermal gravimetric analysis shows a weight loss of 11.28% with an onset at 117 °C (close to the calculated value of 11.78% for the loss of the 6 non-coordinated DMF molecules), a further weight loss of 13.86% at 197 °C, decomposition at 320 °C and the residue at 800 °C is 26.33% of the initial mass. Assuming the residue is pure Co₃O₄ gives an experimental mass for Co of 19.33%, in good agreement with the calculated value.

S1.5 Synthesis of [Co₃(Chrysazinate)₂(AcO)₂DMF₃Pyridine] (CoChrys-2)

Co(AcO)₂·4H₂O (266 mg, 1.07 mmol), chrysazin (176 mg, 0.53 mmol), pyridine (100 µl) and DMF (10 ml) were placed in a 20 ml vial (giving a 2:1 metal:ligand molar ratio). The vial was placed in an oven at 90 °C for 7 days. After this time the vial was removed from the oven and allowed to cool to room temperature. The solid was

recovered by Büchner filtration and washed on the filter with approximately 10 ml each of DMF and ethanol. Black block-shaped crystals were collected (Yield: 30 mg, 16% with respect to chrysazin). Elemental analysis: Calculated mass %: C 51.65; H 4.15; N 5.24; Co 16.53; O 22.44. Found mass %: C 51.41; H 4.20; N 5.27.

S1.6 Synthesis of $2[\text{Co}_4(\text{Chrysazinate})_4\text{DMF}_4]\cdot 2.35(\text{DMF})\cdot \frac{1}{2}\text{H}_2\text{O}$ (CoChrys-3)

DMF was deaerated by bubbling N_2 for 1 hour. $\text{Co}(\text{OH})_2$ (29.7 mg, 0.32 mmol) and chrysazin (52.8 mg, 0.16 mmol) were placed in a 20 ml vial (giving a 1:1 metal:ligand molar ratio). 10 ml of deaerated DMF was added and the vial flushed with N_2 for 30 seconds. The vial was placed in an oven at 90°C for 17 days. After this time the vial was removed from the oven and allowed to cool to room temperature. Small, dark red, plate-like crystals were observed and the structure of these crystals was solved from data collected at the National Crystallography Service, Southampton, UK. This procedure has proved difficult to reproduce.

S1.7 Synthesis of $[\text{Ni}_{12}(\text{Chrysazinate})_6(\text{AcO})_{12}\text{DMF}_6]\cdot 6(\text{DMF})$ (NiChrys-1)

A stock solution of $\text{Ni}(\text{AcO})_2\cdot 4\text{H}_2\text{O}$ (709.1 mg) in DMF (85.5 ml) was prepared. Chrysazin (24 mg, 0.1 mmol) and DMF (1 ml) were placed in a 20 ml glass vial and the $\text{Ni}(\text{AcO})_2\cdot 4\text{H}_2\text{O}$ stock solution (6 ml) was added (giving a 2:1 metal:ligand molar ratio). The vial was placed in an oven at 90°C for 34 hours. After this time the vial was removed from the oven and allowed to cool to room temperature. The solid was recovered by Büchner filtration and washed on the filter with approximately 10 ml each of DMF and ethanol. Black block-shaped crystals were collected (Yield: 40 mg, 64% with respect to chrysazin). Elemental analysis: Calculated mass % (based on six non-coordinated DMF molecules per molecule of $\text{Ni}_{12}\text{Chrysazin}_6(\text{AcO})_{12}\text{DMF}_6$): C 46.46; H 4.22; N 4.52; Ni 19.01; O 25.79. Found mass %: C 46.00; H 4.24; N 4.64. Thermal gravimetric analysis shows a weight loss of 11.51% with an onset at 78°C (which agrees well with the calculated value of 11.8% for the loss of the 6 non-coordinated DMF molecules), a further weight loss of 11.51% at 204°C , and the residue at 800°C is 24.47% of the initial mass. Assuming the residue is pure NiO gives an experimental mass for Ni of 19.25%, in good agreement with the calculated value (19.01%).

S1.8 Synthesis of $[\text{Ni}_6(\text{Chrysazinate})_4(\text{AcO})_4\text{DMF}_4]\cdot 2(\text{DMF})$ (NiChrys-2)

Stock solutions of $\text{Ni}(\text{AcO})_2\cdot 4\text{H}_2\text{O}$ (709.1 mg) in DMF (85.5 ml) and chrysazin (840.7 mg) in DMF (35 ml) were prepared. $\text{Ni}(\text{AcO})_2\cdot 4\text{H}_2\text{O}$ stock solution (3.6 ml) and chrysazin stock solution (1 ml) were mixed in a 10 ml glass vial (giving a 1.2:1 molar metal:ligand ratio). The vial was placed in an oven at 90°C for 18 hours. After this time the vial was removed from the oven and allowed to cool to room temperature. The product was predominantly **NiChrys-1**; however, red block-shaped crystals of **NiChrys-2** were picked out of solution and the structure determined by single-crystal X-ray diffraction. It has not been possible to synthesise a phase-pure sample of **NiChrys-2**.

S1.9 Synthesis of $[\text{Cu}_2(\text{Chrysazinate})_2]$ (CuChrys-1)

Stock solutions of $\text{Cu}(\text{AcO})_2\cdot \text{H}_2\text{O}$ (513.8 mg) in DMF (80 ml) and chrysazin (313.8 mg) in DMF (80 ml) were prepared. The $\text{Cu}(\text{AcO})_2\cdot \text{H}_2\text{O}$ solution (5 ml) was mixed with the chrysazin solution (5 ml) in a 20 ml glass vial (giving a 2:1 metal:ligand molar ratio and a chrysazin concentration of 0.008 mmol/ml). The vial was placed in an oven at 90°C for 48 hours. After this time the vial was removed from the oven and allowed to cool to room temperature. The solid was recovered by Büchner filtration and washed on the filter with approximately 10 ml each of DMF and ethanol. Black plate-like crystals were collected (Yield: 14 mg, 56% with respect to chrysazin). Elemental analysis: Calculated mass %: C 55.73; H 2.00; N 0.00; Cu 21.06; O 21.21. Found mass %: C 55.39;

	C-O bond lengths (Å)	
	CuChrys-1	Chrysazin
C-O 1&8	1.295	1.361
	1.298	
	1.299	
	1.299	
C-O 9	1.305	1.225
	1.312	
C-O 10	1.231	1.171

Table S1 C-O bond lengths for **CuChrys-1** compared to chrysazin. Chrysazin bond lengths taken from the Cambridge Structural Database entry DHANQU07. The errors in these bond lengths are in the region of 1×10^{-3} to 4×10^{-3} Å.

H 2.24; N 0.39. Thermal analysis shows a single decomposition at 303 °C and the residue at 800 °C is 26.60%. Assuming the residue is pure CuO gives an experimental mass for Cu of 20.92%, in good agreement with the calculated value (21.06%).

For the reactions over different times, the above procedure was used and vials were removed from the oven after 1, 3, 18 and 48 hours. Immediately after the vial was removed from the oven, the products were filtered off and a PXRD pattern was taken.

For pure chrysazin the C-O bonds can be clearly assigned as quinone or phenol-type bonds, as the C-O bonds in positions 1 & 8 are significantly longer than those in positions 9 & 10 (Fig. 1). However, comparing the C-O bond lengths in chrysazin and **CuChrys-1** shows that when chrysazin is deprotonated and coordinates to copper, the dianion is delocalised over the 3 coordinating oxygens and the bond lengths become more equal so the bonds have a bond order between 1 and 2 (Table S1). The IR spectrum of **CuChrys-1** shows that there are no hydroxyl groups present consistent with the assignment of the O10 as belonging to a carbonyl group (Fig. S2). This observation further confirms that the oxidation state has been correctly assigned from the XRD data.

S1.10 Synthesis of $[\text{Cu}_2(\text{Chrysazinate})_2] \cdot 0.44\text{DMF}$ (**CuChrys-2**)

The same procedure as for **CuChrys-1** was followed, but the reaction was stopped after times ranging from 1-18 hours. Black needle like crystals could be picked out from a mixture of **CuChrys-1** and, for shorter reaction times, **CuChrys-4**. It has not been possible to synthesise a phase-pure sample of **CuChrys-2**.

S1.11 Synthesis of $[\text{Cu}_2(\text{Chrysazinate})_2\text{DMSO}_2]$ (**CuChrys-3**)

Stock solutions of $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$ (479.2 mg) in DMF (80 ml) and chrysazin (288.24 mg) in DMSO (80 ml) were prepared. The $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$ solution (5 ml) was mixed with the chrysazin solution (5 ml) in a 20 ml glass vial (giving a 2:1 metal:ligand molar ratio). The vial was placed in an oven at 90 °C for 7 days. After this time the vial was removed from the oven and allowed to cool to room temperature. The solid was recovered by Büchner filtration and washed on the filter with approximately 10 ml each of DMF and ethanol. Black, square plate-like crystals were collected. It has not been possible to synthesise a phase-pure sample of **CuChrys-3**.

S1.12 Synthesis of [Cu(HChrysazinate)₂] (CuChrys-4)

Stock solutions of Cu(AcO)₂·H₂O (513.8 mg) in DMF (80 ml) and chrysazin (313.8 mg) in DMF (80 ml) were prepared. The Cu(AcO)₂·H₂O solution (1.08 ml) was mixed with the chrysazin solution (8.92 ml) in a 20 ml glass vial (giving a 2:1 metal:ligand molar ratio). The vial was placed in an oven at 90 °C for 18 hours. After this time the vial was removed from the oven and allowed to cool to room temperature. The solid was recovered by Büchner filtration and washed on the filter with approximately 10 ml each of DMF and ethanol. Red powder was collected. Elemental analysis: Calculated mass %: C 62.05; H 2.60; N 0.00; Cu 11.73; O 233.62. Found mass %: C 61.86; H 2.85; N 0.47.

S1.13 Synthesis of [Ni₂(1,5-dihydroxy-4,8-dinitroanthraquinone)₂DMF₄] (NiNOChrys-1)

Ni(AcO)₂·4H₂O (24.9 mg, 0.1 mmol), 1,5-dihydroxy-4,8-dinitroanthraquinone (33.0 mg, 0.1 mmol), pyrazine (8.0 mg) and DMF (10 ml) were placed in a 20 ml vial (giving a 1:1 metal:ligand molar ratio). The vial was placed in an oven at 90 °C for 14 hours. After this time the vial was removed from the oven and allowed to cool to room temperature. The solid was recovered by Büchner filtration and washed on the filter with approximately 10 ml each of DMF and ethanol. A small amount of red square-platelet crystals were collected; the structure of these crystals was solved from data collected at the National Crystallography Service, Southampton, UK.

S1.14 High-throughput synthesis

The high-throughput technique has been reported previously.^{1,2} High throughput reactions were carried out to screen each of the transition metal salts in Table S2 against reaction with chrysazin in DMF. Table S2 also gives the values that were used for the ligand:metal molar ratios and the concentrations of ligand + metal. In each case the solid reagents (c. 2-20 mg) were weighed into a 2 ml Teflon container and 1 ml DMF was added. These Teflon containers were inserted into one of the 24 wells in the high-throughput reactor, which was then sealed and placed in an oven at 90 °C for 16 hours. After this time the reactor was removed from the oven and allowed to cool to room temperature. The reagents were filtered using a high-throughput filter block and characterised by XRD using a Stoe Stadi P diffractometer in transmission geometry with Cu K α ₁ radiation, equipped with an image-plate detector and an x-y stage sample changer. No solid products were found in the reaction with Fe(AcO)₂ or Mn(AcO)₂·4H₂O.

Metal salts	Ligand:metal ratio	[metal + ligand] mmol/ml
Mn(AcO) ₂ ·4H ₂ O	3:1	0.016
Fe(AcO) ₂	2:1	0.04
Co(AcO) ₂ ·4H ₂ O	1:1	0.16
Ni(AcO) ₂ ·4H ₂ O	1:1.5	0.4
Cu(AcO) ₂ ·H ₂ O	1:2	
	1:3	

Table S2 Parameters used in the high-throughput screening reactions with chrysazin.

S1.15 Treatment of CuChrys-1 with hydrogen gas

Powdered **CuChrys-1** was placed in a tube furnace and left under a flow of 5% H₂ in N₂ for 18 hours at either 20 °C or 150 °C. At 20 °C there was no change in the material observable by PXRD; at 150 °C the material

reacted to form **CuChrys-4** and copper.

S1.16 Single-crystal X-ray diffraction (SCXRD)

For all compounds except **CoChrys-3**, **CuChrys-2** and **NiNOChrys-1**, each crystal was mounted on a cryo-loop and single-crystal X-ray diffraction data was collected on an Xcalibur Gemini ultra diffractometer fitted with an Eos CCD detector. Data were collected using Cu K α or Mo K α at temperatures between 100 K and 270 K (see Tables S3 to S5). Analytical absorption corrections were applied as implemented in CrysAlisPro.³ For compounds **CoChrys-3**, **CuChrys-2** and **NiNOChrys-1**, data was collected via the National Crystallographic Service.⁴ Data for **CoChrys-3** and **NiNOChrys-1** was collected at 100 K using Mo K α_1 radiation on a Rigaku FR-E+ Very High Flux Diffractometer equipped with a Saturn724+ detector. Data for **CuChrys-2** was collected at Diamond Light Source (beamtime award MT8521) on I19 and a multi-scan absorption correction applied. Using Olex2⁵, the structures were solved with the ShelXS⁶ structure solution program using Direct Methods, except for **NiChrys-2** which was solved using the program Superflip⁷ using Charge Flipping. Structures were then refined with the ShelXL⁶ refinement package using Least Squares minimisation. Hydrogen atoms were added geometrically and refined using isotropic displacement parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. Detailed information about the modelling of disorder and the treatment of unresolved electron density is contained in the crystallographic information files (CCDC 1044027-1044037).

S1.17 Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) was carried out on a Philips PW 1830 generator fitted with Cu K α_1 X-ray source, a point detector and a secondary beam monochromator.

S1.18 High-throughput PXRD

High-throughput PXRD data were obtained using a Stoe Stadi P diffractometer in transmission geometry with Cu K α_1 radiation, equipped with an image-plate detector and an x-y stage sample changer.

S1.19 DC conductivity & AC impedance measurements on **CuChrys-1**

AC impedance was used to assess the conductivity of **CuChrys-1** using a Gamry Interface 1000 instrument over the frequency range of 1 MHz to 0.1 Hz and at an AC amplitude of 1000 mV. Pressed-powder pellets were made by gently grinding the samples to a fine powder using a pestle and mortar. 100 mg of ground sample was placed in a 10 mm diameter die and subjected to a 2 ton load for 10 minutes in a pellet press. The pressed-pellet was carefully transferred to a commercially available cell with brass electrodes covered with a thin gold layer (EQ-STC 10 mm, MTI Corporation, USA). Single-crystal conductivity was measured using gold microelectrodes evaporated onto a quartz substrate with a spacing of 80 μm , as reported previously.⁸ Single crystals were mounted across the electrodes and pressed into conformal contact using electrically insulating, silicone adhesive tape. The crystals were checked for mechanical damage before and after the measurement using optical microscopy. The resistance of **CuChrys-1** was at least as large as the apparent resistance of the blank resistance of the measurement setup, i.e. the sample was insulating. This observation, combined with measurements of the powder pellet dimensions, allows us to place an upper bound of the conductivity of **CuChrys-1** of $2 \times 10^{-12} \text{ S cm}^{-1}$.

S1.20 Density functional theory calculations

We carried out plane-wave pseudopotential DFT⁹⁻¹¹ calculations as implemented in the CASTEP package¹². We used the local density approximation (LDA)^{13,14} to the exchange-correlation functional and “on-the-fly” ultrasoft pseudopotentials¹⁵. As calculation parameters we used a kinetic energy cut-off of 400 eV and a Monkhorst-Pack¹⁶ Brillouin zone sampling density $2\pi \times 0.03 \text{ \AA}^{-1}$. Starting from the experimentally determined structure, we relaxed the cell parameters to reduce the stress below 4×10^{-2} GPa, and we also relaxed the internal atomic coordinates to reduce the forces on the atoms below 5×10^{-2} eV/Å. For the high-pressure calculations we relaxed the structures in the presence of the appropriate external pressures, with the residual stresses and forces reduced to similar magnitudes as those in the zero-pressure case. We then calculated band structures and electronic densities of states (DOS) using the OPTADOS package^{17,18}. We used adaptive broadening in order to achieve accurate DOS and partial DOS¹⁹.

S2 Supplementary data

S2.1 Single-crystal data summary

Table S3 Crystallographic data for the reported compounds.

Phase	FeChrys-1	FeChrys-2	CoChrys-1	CoChrys-2
Formula	[Fe(HChrysazinate) ₂ DMF ₂]	[Fe ₂ (Chrysazinate) ₃] ·DMF· $\frac{1}{2}$ H ₂ O	[Co ₁₂ (Chrysazinate) ₆ (AcO) ₁₂ DMF ₆]·6(DMF)	[Co ₃ (Chrysazinate) ₂ (AcO) ₂ DMF ₃ Pyridine]
Formula unit	C ₃₄ H ₂₈ FeN ₂ O ₁₀	C ₄₅ H ₂₆ Fe ₂ NO _{13.5}	C ₁₄₄ H ₁₅₆ Co ₁₂ N ₁₂ O ₆₀	C ₄₆ H ₄₄ N ₄ O ₁₅ Co ₃
Formula weight	680.43	908.40	3721.96	1069.64
Crystal system	monoclinic	triclinic	trigonal	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>R</i> $\bar{3}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	10.0131(4)	8.2927(4)	28.6873(9)	12.3354(5)
<i>b</i> /Å	8.4169(4)	15.5166(7)	28.6873(9)	12.8534(7)
<i>c</i> /Å	18.1414(8)	15.8042(6)	15.9087(10)	14.3146(5)
α /°	90	118.226(4)	90	91.265(4)
β /°	100.448(4)	92.344(4)	90	97.978(3)
γ /°	90	92.239(4)	120	94.724(4)
Volume/Å ³	1503.60(12)	1786.33(15)	11338.2(10)	2238.72(18)
<i>Z</i>	2	2	3	2
ρ_{calc} mg/mm ³	1.503	1.689	1.635	1.587
Temperature/K	270	120	120	120
Radiation	Cu K α (λ = 1.5418)	CuK α (λ = 1.5418)	MoK α (λ = 0.7107)	Mo K α (λ = 0.7107)
Independent reflections	2679[R _{int} = 0.0265]	6352[R _{int} = 0.0282]	5582[R _{int} = 0.0725]	8806[R _{int} = 0.0226]
R ₁ , wR ₂ [I ≥ 2(I)]	0.0385, 0.1113	0.0516, 0.1440	0.0538, 0.1140	0.0298, 0.0675
Colour	Black	Red	Black	Black
Powder colour	?	?	Red	Red

Table S4 Crystallographic data for the reported compounds.

Phase	CoChrys-3	NiChrys-1	NiChrys-2	CuChrys-1
Formula	2[Co ₄ (Chrysazinate) ₄ DMF ₄]·2.35(DMF)· $\frac{1}{2}$ H ₂ O	[Ni ₁₂ (Chrysazinate) ₆ (AcO) ₁₂ DMF ₆]·6(DMF)	[Ni ₆ (Chrysazinate) ₄ (AcO) ₄ DMF ₄]·4(DMF)]	[Cu ₂ Chrysazinate ₂]
Formula unit	C _{143.05} H _{120.45} N _{10.35} O _{42.85} Co ₈	C ₁₄₄ H ₁₅₆ N ₁₂ Ni ₁₂ O ₆₀	C ₈₈ H ₉₂ N ₈ Ni ₆ O ₃₂	C ₂₈ H ₁₂ Cu ₂ O ₈
Formula weight	3141.48	3719.32	2125.95	603.46
Crystal system	triclinic	trigonal	triclinic	monoclinic
Space group	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$	$P2_1/c$
a/Å	15.6278(16)	28.6809(7)	9.7302(6)	13.5308(3)
b/Å	15.6996(15)	28.6809(7)	13.4388(5)	7.7288(2)
c/Å	29.048(3)	15.8967(4)	17.0848(7)	19.6854(4)
$\alpha/^\circ$	90.9201(10)	90	95.504(3)	90
$\beta/^\circ$	104.1390(16)	90	97.873(4)	99.380(2)
$\gamma/^\circ$	90.2340(13)	120	95.172(4)	90
Volume/Å ³	6909.8(12)	11324.6(6)	2190.66(18)	2031.10(9)
Z	2	3	1	4
ρ_{calc} mg/mm ³	1.510	1.636	1.611	1.973
Temperature/K	100	120	200	120
Radiation	MoK α ($\lambda = 0.7107$)	CuK α ($\lambda = 1.5418$)	CuK α ($\lambda = 1.5418$)	CuK α ($\lambda = 1.5418$)
Independent reflections	31716[R _{int} = 0.0512]	4851[R _{int} = 0.0250]	7058[R _{int} = 0.0294]	3926[R _{int} = 0.0220]
R ₁ , wR ₂ [I ≥ 2(I)]	0.0627, 0.1829	0.0291, 0.0847	0.0598, 0.1810	0.0314, 0.0921
Colour	Dark red	Black	Red	Black
Powder colour	Dark red	Red	Red	Black

Table S5 Crystallographic data for the reported compounds. **CuChrys-3** was solved in a non-centrosymmetric space group; the Flack parameter for the refinement was 0.023(14).

Phase	CuChrys-2	CuChrys-3	NiNOChrys-1
Formula	[Cu ₂ (Chrysazinate) ₂] ·0.44DMF	[Cu ₂ (Chrysazinate) ₂ DMSO ₂]	[Ni ₂ (4,5-dinitrochrysazinate) ₂ DMF ₄]
Formula unit	C _{29.33} H _{15.11} Cu ₂ N _{0.44} O _{8.44}	C ₃₂ H ₂₄ O ₁₀ S ₂ Cu ₂	C ₄₀ H ₃₆ N ₈ Ni ₂ O ₂₀
Formula weight	635.77	759.71	1066.19
Crystal system	trigonal	orthorhombic	monoclinic
Space group	$R\bar{3}$	$Pca2_1$	$P2_1/n$
a/Å	40.04(3)	7.90242(16)	9.5780(7)
b/Å	40.04(3)	19.4909(4)	11.0933(8)
c/Å	3.674(3)	18.5266(4)	20.1508(14)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	90	90	99.517(6)
$\gamma/^\circ$	120	90	90
Volume/Å ³	5101(9)	2853.56(10)	2111.6(3)
Z	9	4	2
ρ_{calc} mg/mm ³	1.863	1.768	1.677
Temperature/K	100	120	100
Radiation	synchrotron ($\lambda = 0.6889$)	CuK α ($\lambda = 1.5418$)	MoK α ($\lambda = 0.7107$)
Independent reflections	2587[R _{int} = 0.068]	4714[R _{int} = 0.0307]	4719[R _{int} = 0.1057]
R ₁ , wR ₂ [I ≥ 2(I)]	0.0503, 0.1295	0.0378, 0.0996	0.0754, 0.1413
Colour	Black	Black	Black
Powder colour	Black	Red	Purple

S2.2 PXRD

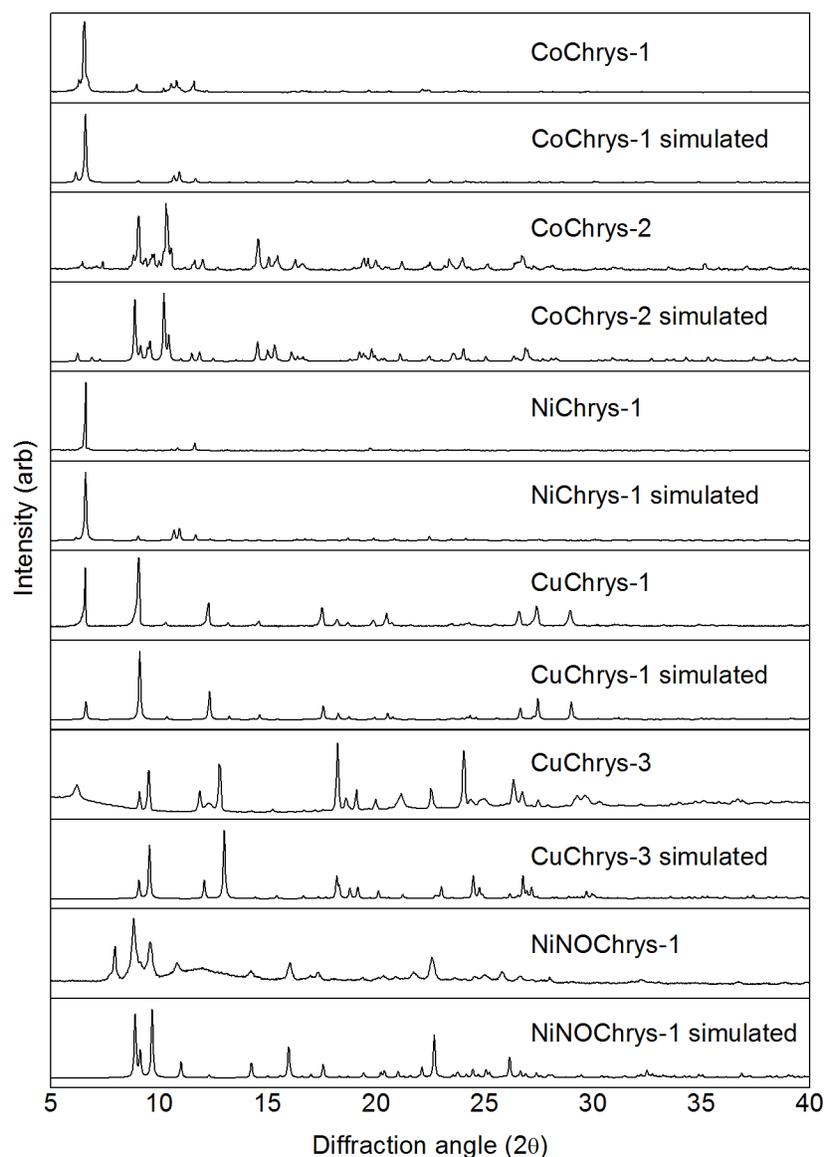


Figure S1 PXRD data for the phases found in this study. **CoChrys-1** and **CoChrys-2** show peak splitting, indicating that the phases are not structurally pure (this worsens with progressive grinding during preparation for PXRD, or standing in air); the fact that the elemental analysis of these phases is consistent with the expected formula suggests that the material is compositionally pure, but undergoes structural transformation/degradation. **NiChrys-1** suffers the same problems; however, we obtained a pure PXRD pattern by grinding the crystals gently in a small amount of mother liquor and taking a PXRD pattern of this paste. The products **CuChrys-3** and **NiNOChrys-1** show peaks that are not due to the known compound; unfortunately, it has not been possible to purify these samples or to identify the unknown phases.

S2.3 IR data

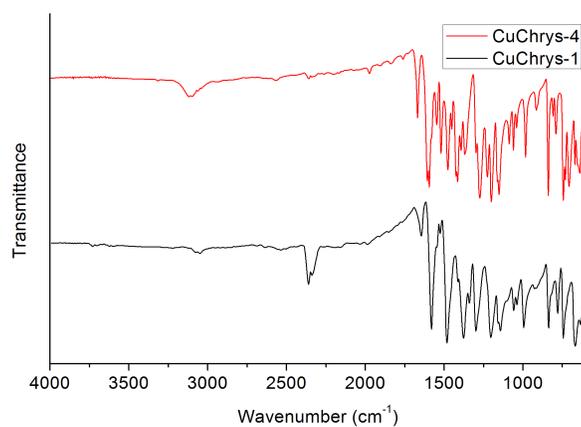


Figure S2 IR spectra of **CuChrys-1** and **CuChrys-4**. The spectrum for **CuChrys-4** shows a broad peak at 3120 cm⁻¹, which we attribute to a protonated hydroxyl group, not present in **CuChrys-1**.

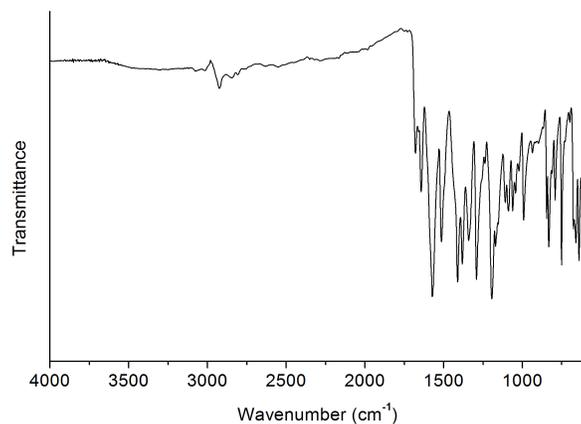
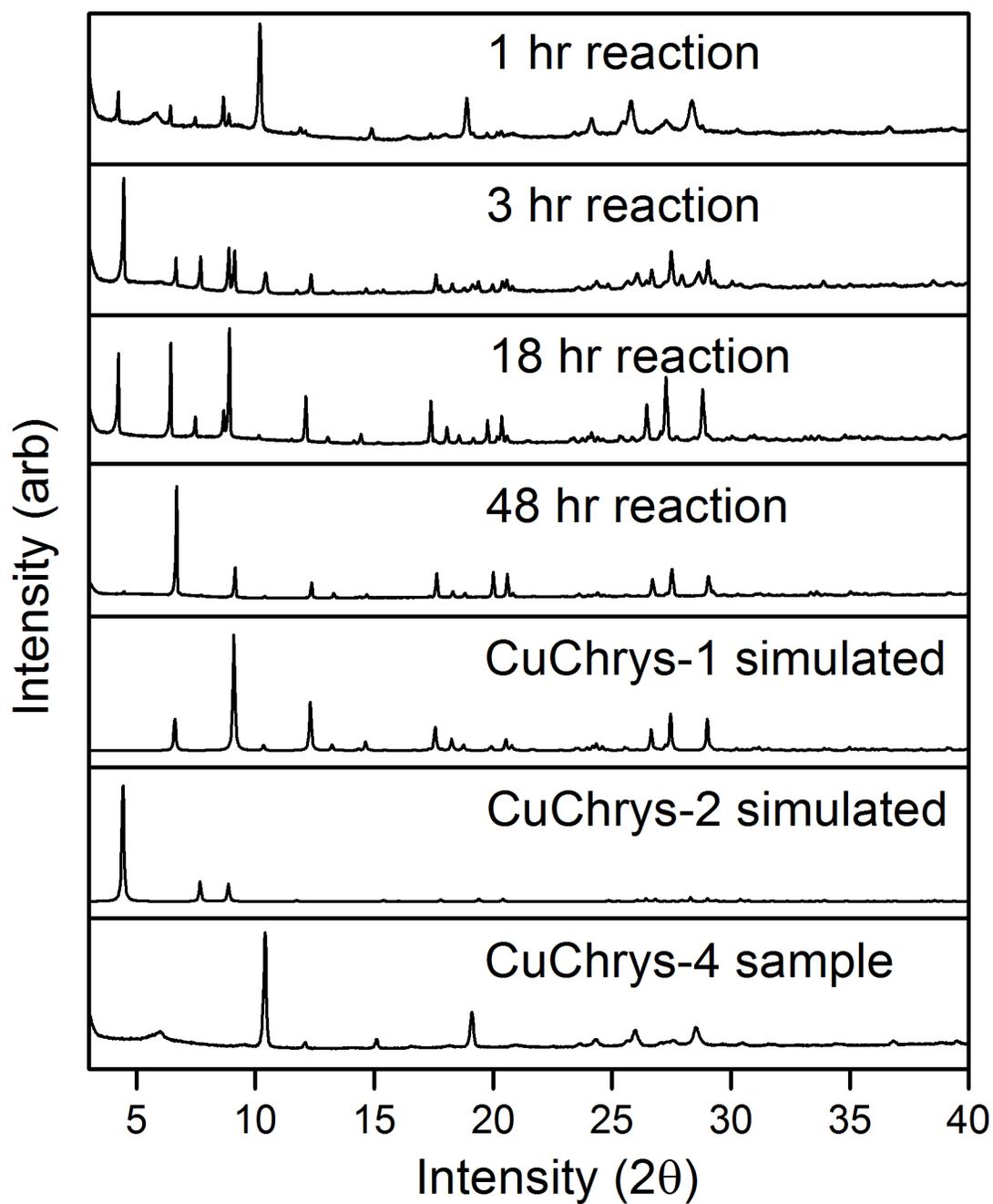


Figure S3 IR spectra of **CoChrys-1**. The spectrum shows a strong peak at 1677 cm⁻¹ in good agreement with the expected position for the C=O stretch of DMF (1675 cm⁻¹). No O-H stretching peak is observed. These observations support our conclusion that the included solvent is DMF rather than water.

S2.4 Evolution of the reaction between $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$ and chryszin over time**Figure S4** PXR D patterns of the products of the reaction between $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$ and chryszin in DMF at different times.

S2.5 Reaction of CuChrys-1 with H₂

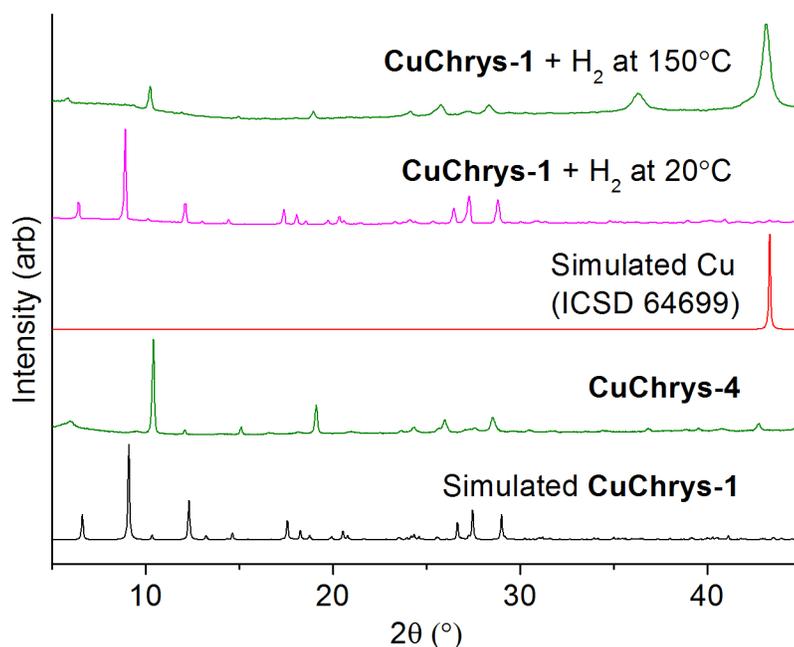


Figure S5 PXRD patterns showing the products of reaction of **CuChrys-1** with H₂ gas (5% v/v in N₂). **CuChrys-1** reacts to form **CuChrys-4** and elemental copper.

S2.6 Effect of pressure on the band structure of CuChrys-1

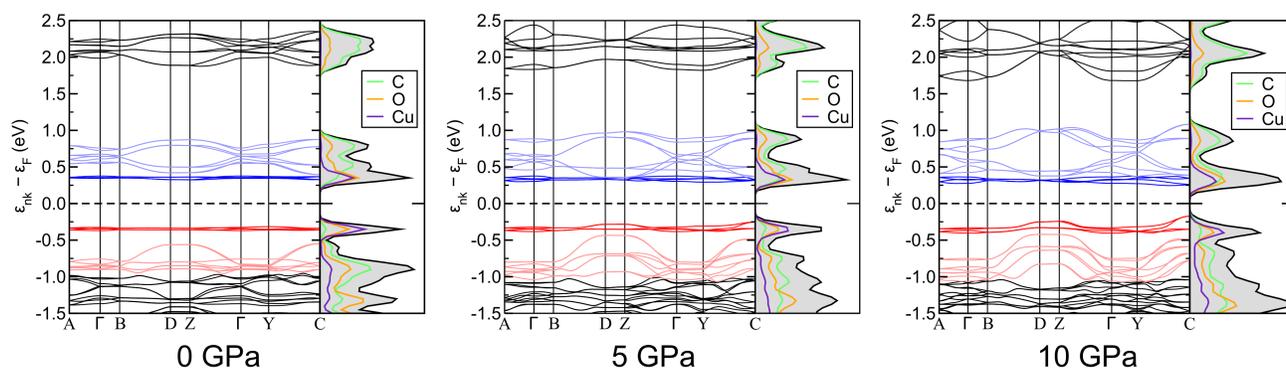


Figure S6 DFT calculations with different externally applied pressures. The disperse bands above the LUMO and below the HOMO become more dispersed at increased pressure, though not enough to change the order of the energy levels/bands.

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