

Supporting Information

Cobalt(II) - Pyrazine-Chloride Coordination Polymers: Synthesis, Reactivity and Magnetic Properties

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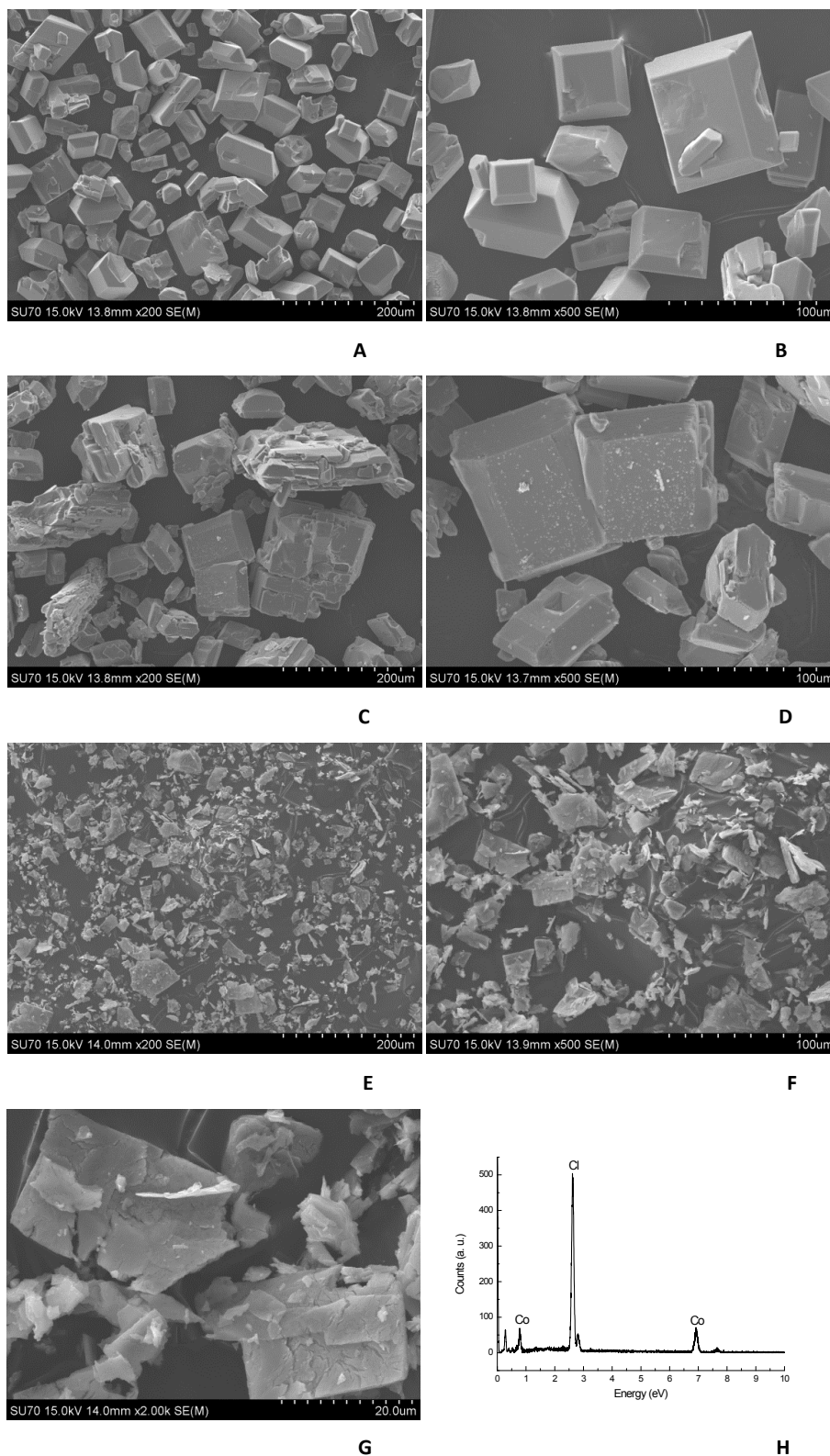


Figure S1: SEM images of $[\text{CoCl}_2\text{pyz}]_n$ obtained by (A) and (B) non-stoichiometric procedure; (C) and (D) stoichiometric procedure; (E), (F) and (G) thermal decomposition of $[\text{CoCl}_2(\text{pyz})_2]_n$. The EDS spectrum in (H) is from the compound obtained by the stoichiometric procedure, and that is very similar to the spectra of compounds obtained by other procedures.

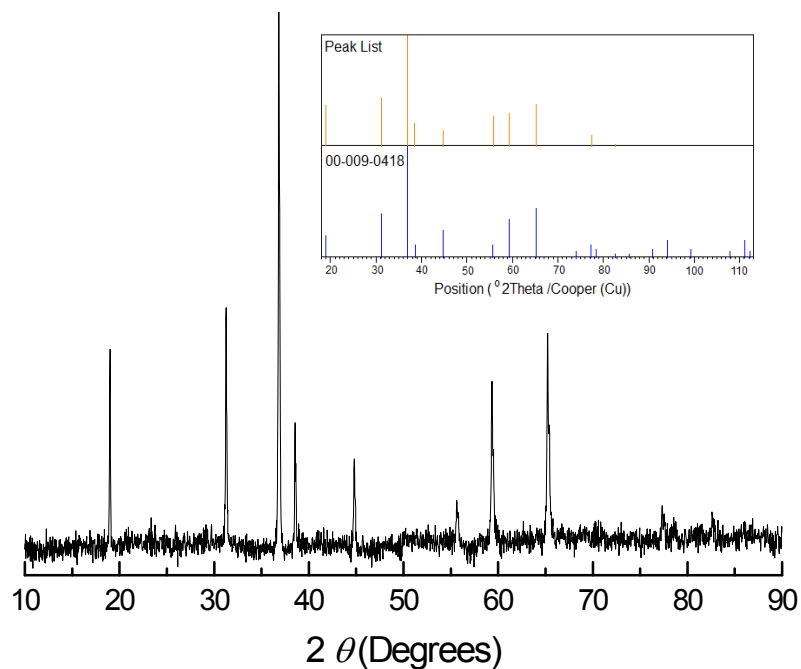


Figure S2: XRD of the product of the thermal decomposition of $[\text{CoCl}_2\text{pyz}]_n$. The inset compares the peaks position and intensity with those of standard Co_3O_4 .

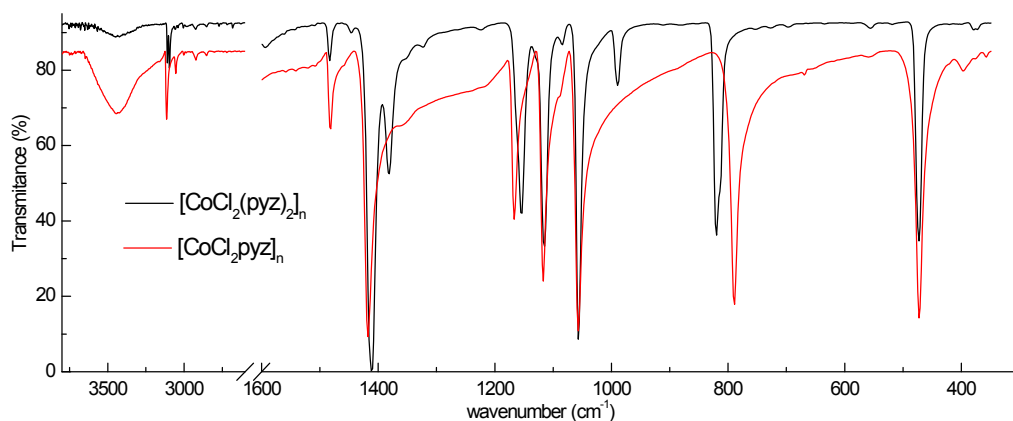


Figure S3: Infrared spectra of $[\text{CoCl}_2\text{pyz}]_n$ obtained by non-stoichiometric procedure and $[\text{CoCl}_2(\text{pyz})_2]_n$ obtained according Ref. 1.

Details of the fit shown in Figure 6 of manuscript

$[\text{CoCl}_2(\text{pyz})_2]_n$ was successfully modelled as a mononuclear system containing high-spin Co(II) ions in distorted octahedral environments. Within the studied temperature range interactions between the Co(II) ions are not apparent, which, of course, does not rule out their appearance at lower temperatures. The lowest-energy states of such Co(II) ions are Γ_6 and Γ_7 doublets and, on a first approximation, it may be considered that only these two states are thermally populated. The Hamiltonian may be written as

$$\mathbf{H} = \Delta(\mathbf{L}_z^2 - 2/3) - (3/2)\kappa\lambda\mathbf{L}\cdot\mathbf{S} + \beta[-(3/2)\kappa\mathbf{L}_u + g_e\mathbf{S}_u] \cdot \mathbf{H}_u \quad (\text{Eq. S1})$$

where the first term is the operator associated to the tetragonal distortion of the octahedral Co(II) environment (Δ is the associated energy gap in the absence of any spin-orbit coupling), the second term is the spin-orbit operator and the third term is the Zeeman operator.^{S1} Here, κ is the orbital reduction factor

and λ is the spin-orbit coupling that may be different from the free-ion value to account for covalence and ligand-field effects. This Hamiltonian may be diagonalized in the M_L, M_S basis. The susceptibility may then be determined using the Van Vleck approximation^{S2} or numerically (see, e.g., ref. [24]). The recently released programme PHI was used to perform this task and fit the susceptibility of $[\text{CoCl}_2(\text{pyz})_2]_n$ (Figure 6, manuscript). The susceptibility data are well reproduced with $\lambda = -91 \text{ cm}^{-1}$, $\kappa = 1$ and $\Delta = -250 \text{ cm}^{-1}$. The fitted λ implies a reduction to about 0.5 of the free ion value ($\lambda_0 = -171.5 \text{ cm}^{-1}$) being lower than the value expected for Co(II) ions in distorted octahedral environments,²² while the orbital contribution is not reduced (as usually observed in Co(II) salts)^{22, 25} yielding an high temperature effective moment close to $5.2 \mu_B$. The best fit is obtained with $\Delta = -250 \text{ cm}^{-1}$, while positive values, lower in absolute value ($\Delta = +120 \text{ cm}^{-1}$), yield a fit with quality similar to what was previously observed.²²

In- and out-of-phase magnetic susceptibility of $[\text{CoCl}_2\text{pyz}]_n$

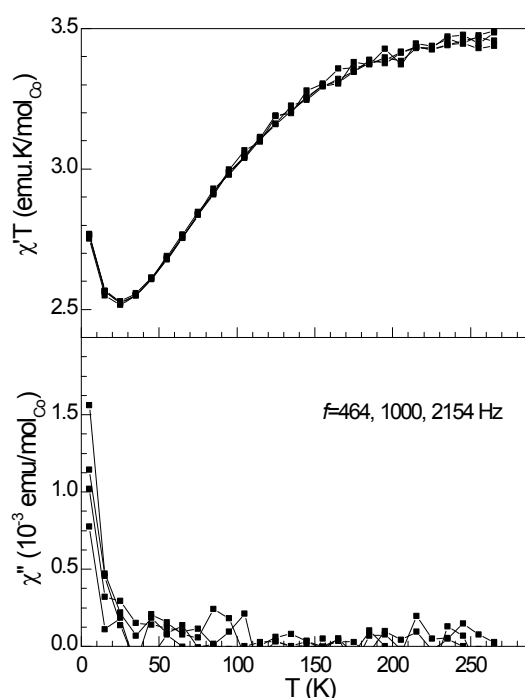


Figure S4 (a) top - $[\text{CoCl}_2\text{pyz}]_n$ temperature dependence of the in-phase magnetic susceptibility multiplied by temperature ($\chi'T$ vs. T) at the frequencies depicted. **(b) bottom** - $[\text{CoCl}_2\text{pyz}]_n$ temperature dependence of the out-of-phase magnetic susceptibility χ'' at the frequencies depicted. Lines are guides to the eye. A small on-set of χ'' below *ca.* 30 K and a small frequency dependence of χ' are clearly observed. However, compared to the tail observed in $\chi'T$ this constitutes a small feature in line with that previously observed in Co(II) ferromagnetic chains [S3].

References

- S1. O. Kahn, *Molecular Magnetism*, Wiley-VCH, New York, 1993, ch. 3, pp. 38-42.
- S2. B.N. Figgis, M. Gerloch, J. Lewis, F.E. Mabbs, G.A. Webb, *J. Chem. Soc. A*, 1968, 2086.
- S3. J. M. Clemente-Juan, E. Coronado, G. M. Espallargas, H. Adams, L. Brammer, *Cryst. Eng. Comm.*, 2010, **12**, 2339.