Electronic Supplementary Information

Synthesis, structure and magnetic properties of phenylhydroxamate-based coordination clusters.

Remi Tirfoin[1], Lise-Marie Chamoreau[1,3], Yanling Li[1,2], Benoit Fleury[1], Laurent Lisnard[1,2], Yves Journaux*[1,2].

Figure S1: powder diffraction pattern measured for **4** and calculated for **3**.

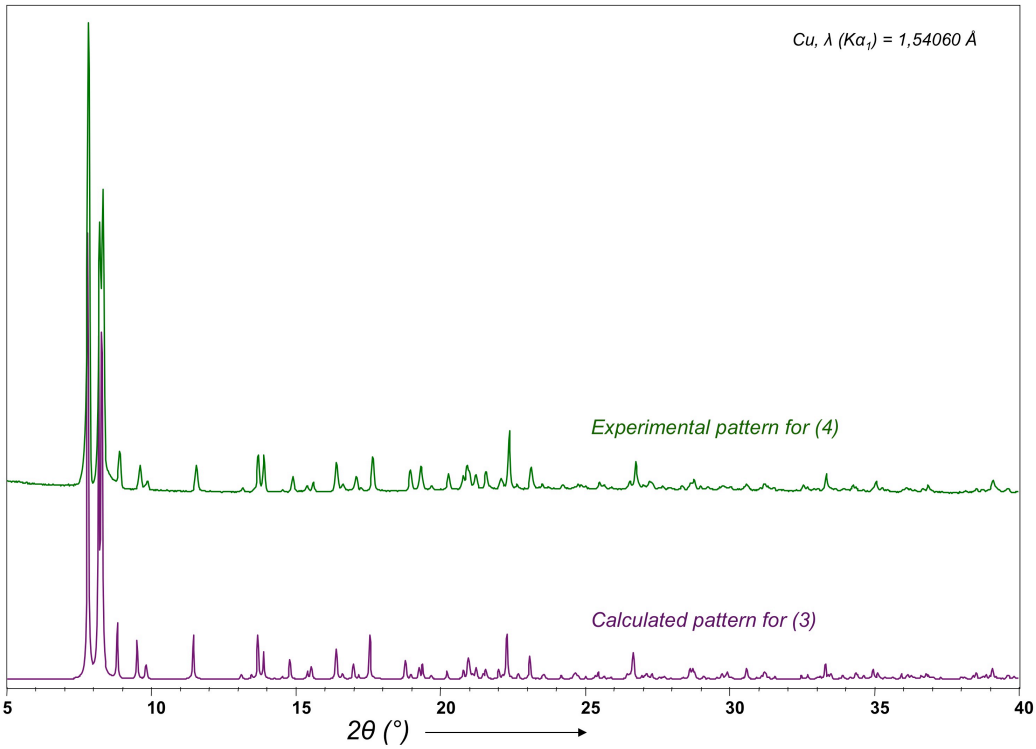


Figure S2: intermolecular interactions in the crystal packing of **3** with orange dotted lines highlighting the H bonds. ^{t}Bu groups and non-water hydrogen atoms have been removed for clarity.

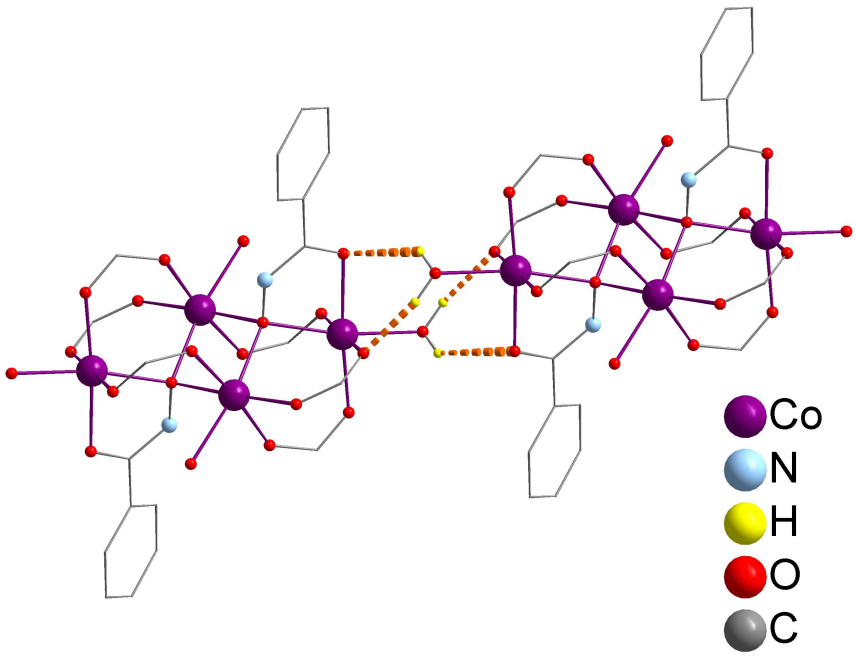


Figure S3: χ_M *vs.* *T* and $1/\chi_M$ *vs.* *T* plots measured at 1 kOe for **1**. The solid black lines are the best-fit curves.

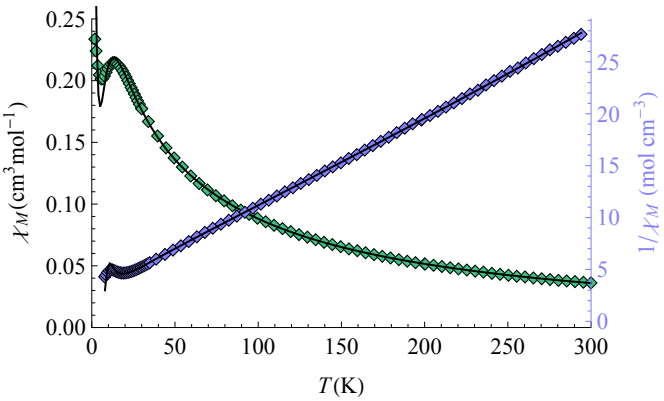


Figure S4: χ_M *vs.* *T* and $1/\chi_M$ *vs.* *T* plots measured at 1 kOe for **2**. The solid black lines are the best-fit curves.

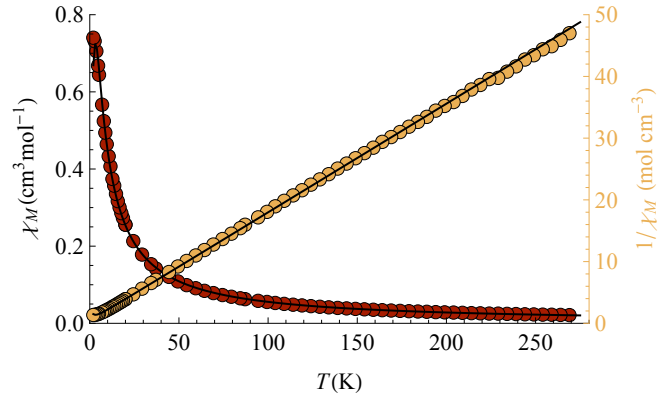


Figure S5: χ_M *vs.* *T* and $1/\chi_M$ *vs.* *T* plots measured at 1 kOe for **3**. The solid black lines are the best-fit curves.

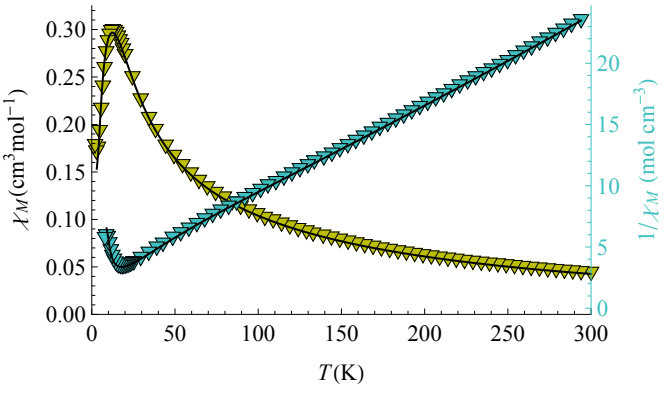


Figure S6: χ_M *vs.* *T* and $1/\chi_M$ *vs.* *T* plots measured at 1 kOe for **4**. The solid black lines are the best-fit curves.

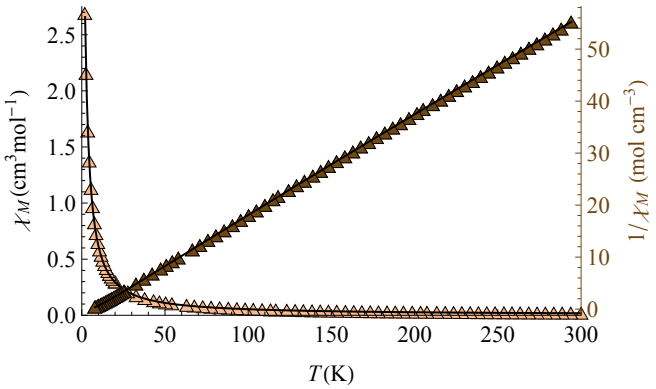
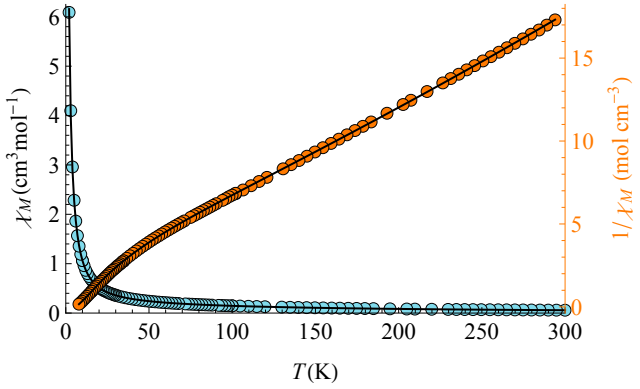


Figure S7: χ_M *vs.* *T* and $1/\chi_M$ *vs.* *T* plots measured at 1 kOe for **5**. The solid black lines are the best-fit curves.



Model used to fit the magnetic data of 1, 3 and 5

To model the magnetic properties of **1**, **3** and **5**, the $\chi_M T$ product is expressed has :

$$\chi_M T = F\left[G_i(T, J_{ij}, \lambda, \alpha, \Delta), T, J_{ij}\right]$$

where **F** is the thermal variation of $\chi_M T$ calculated for a polynuclear system with the same topology than that of **1**, **3** and **5** but with a fictitious $S^{eff}=1/2$ to mimic the ground state Kramer doublet of a Co(II) ion. In order to obtain identical matrix elements in the ground state Kramer's doublet with fictitious $S^{eff}=1/2$ it is necessary to use a 5/3 scaling factor ($S \Rightarrow 5/3\, S_{eff}$). For the butterfly complexes 1 and 3, it is possible to derive an analytical law for F using the Van-Vleck formula.

$$\chi_M T = \left(T \left(\frac{2\,\beta^2\,\mathrm{gbod}^2\, e^{\frac{25\,\mathrm{jwb}}{36\,k\,T}}}{k\,T} - \frac{12\,\beta^2\,(\mathrm{gbod}-\mathrm{gw})^2\, e^{-\frac{\frac{25\,\mathrm{jwb}}{36}-\frac{50\,\mathrm{jbb}}{9}}{k\,T}}}{25\,\mathrm{jbb}} + \right.\right.$$

$$\frac{9\,\beta^2\,(\mathrm{gbod}-\mathrm{gw})^2\, e^{-\frac{\frac{25\,\mathrm{jwb}}{36}-\frac{25\,\mathrm{jbb}}{9}}{k\,T}}}{25\,\mathrm{jbb}} + \frac{3\,\beta^2\,(\mathrm{gbod}-\mathrm{gw})^2\, e^{-\frac{\frac{25\,\mathrm{jbb}}{9}+\frac{25\,\mathrm{jwb}}{36}}{k\,T}}}{25\,\mathrm{jbb}} +$$

$$\frac{2\,\beta^2\,(\mathrm{gbod}+\mathrm{gw})^2\, e^{-\frac{\frac{25\,\mathrm{jbb}}{9}+\frac{25\,\mathrm{jwb}}{36}}{k\,T}}}{k\,T} + 2\, e^{-\frac{\frac{25\,\mathrm{jwb}}{36}-\frac{25\,\mathrm{jbb}}{9}}{k\,T}} \left(\frac{\beta^2\,(\mathrm{gbod}+\mathrm{gw})^2}{4\,k\,T} - \frac{9\,\beta^2\,(\mathrm{gbod}-\mathrm{gw})^2}{100\,\mathrm{jbb}} \right) +$$

$$\left.\left. 2\, e^{-\frac{\frac{25\,\mathrm{jbb}}{9}+\frac{25\,\mathrm{jwb}}{36}}{k\,T}} \left(\frac{9\,\beta^2\,(\mathrm{gbod}-\mathrm{gw})^2}{100\,\mathrm{jbb}} + \frac{\beta^2\,(\mathrm{gbod}+\mathrm{gw})^2}{4\,k\,T} \right) + \frac{2\,\beta^2\,\mathrm{gw}^2\, e^{-\frac{25\,\mathrm{jwb}}{12\,k\,T}}}{k\,T} \right) \right) \Big/$$

$$\left(e^{-\frac{\frac{25\,\mathrm{jwb}}{36}-\frac{50\,\mathrm{jbb}}{9}}{k\,T}} + 3\, e^{-\frac{\frac{25\,\mathrm{jwb}}{36}-\frac{25\,\mathrm{jbb}}{9}}{k\,T}} + 5\, e^{-\frac{\frac{25\,\mathrm{jbb}}{9}+\frac{25\,\mathrm{jwb}}{36}}{k\,T}} + 4\, e^{-\frac{25\,\mathrm{jwb}}{12\,k\,T}} + 3\, e^{\frac{25\,\mathrm{jwb}}{36\,k\,T}} \right)$$

Where j_{bb} and j_{wb} are the body-body and wing-body interaction respectively and g_{bod} and g_w the landé factors of the body and wing ions respectively. The other parameters have their usual meaning.

For **5** the numerical value of **F** is obtained by full diagonalisation of the hamiltonian matrix established using the following hamiltonian :

$$\mathcal{H}_{tot} = \mathcal{H}_{int} + \mathcal{H}_{Ze} \qquad \text{with:}$$

$$\mathcal{H}_{int} = -\frac{25}{9}J_{12}\left(S^{eff}_{Co1a}S^{eff}_{Co2} + S^{eff}_{Co1b}S^{eff}_{Co2}\right) - \frac{25}{9}J_{13}\left(S^{eff}_{Co1a}S^{eff}_{Co3a} + S^{eff}_{Co1b}S^{eff}_{Co3b}\right)$$
$$-\frac{25}{9}J_{14}\left(S^{eff}_{Co1a}S^{eff}_{Co4} + S^{eff}_{Co1b}S^{eff}_{Co4}\right) - \frac{25}{9}J_{23}\left(S^{eff}_{Co2}S^{eff}_{Co3a} + S^{eff}_{Co2}S^{eff}_{Co3b}\right) - \frac{25}{9}J_{24}S^{eff}_{Co2}S^{eff}_{Co4}$$

$$\mathcal{H}_{Ze} = \sum_{i=1}^{6} G_{Coi}\left(T, J_{ij}\right)\beta S_{Coi} H$$

The influence of spin-orbit interaction on each cobalt ion is introduced through a fictitious Landé factor $\mathbf{G}_i$ calculated from the following relation: [F. Lloret et al., *Inorg. Chim. Acta*, 2008, **361**, 3432]

$$G_i(T, J_{ij}) = g(T) + f(J,T)$$

with $f(J,T) = \frac{n}{2}\frac{100J(\alpha+2)}{81\alpha\lambda} P_0$ and $P_0 = \frac{Exp\left[-4\alpha\lambda/k.T\right]}{3+Exp\left[-5\alpha\lambda/2k.T\right]+Exp\left[-4\alpha\lambda/k.T\right]}$

g(T) is calculated using the Curie law for S=1/2 :

$$(\chi_M T)_{Co} = \frac{N\beta^2\, g(T)^2 S(S+1)}{3k} \quad \text{with S} = \frac{1}{2}$$

that is $g(T)^2 = \frac{4k}{N\beta^2}(\chi_M T)_{Co}$

$(\chi_M T)_{Co}$ is an average value obtained with

$$(\chi_M T)_{Co} = \frac{(\chi_{Mz} T)_{Co} + 2(\chi_{Mx} T)_{Co}}{3}$$

$(\chi_{Mx} T)_{Co}$ *and* $(\chi_{Mz} T)_{Co}$ are calculated by full diagonalisation of the hamiltonian matrix established from the following hamiltonian using the T⇔ P isomorphism: [Lines, M. E. *J. Chem. Phys.* 1971, **55**, 2977-2984].

$$\mathcal{H}_v^{SO} = -\frac{3}{2}\alpha\lambda L.S + \Delta\left(L_z^2 - \frac{1}{3}L^2\right) + \left(\frac{-3\alpha}{2}L_v + g_e S_v\right) \quad \text{with } v = x, z$$

where λ the spin-orbit coupling constant, α the orbital reduction factor, Δ the axial distortion parameter and g_e is the giromagnetic ratio of a free electron.
In our case for each Co(II) ions there are different exchange interaction pathways corresponding to different *J* values Therefore to calculate ***f(J,T)*** we used an averaged $J_{i,average}$ values for each cobalt ions according to :

$J_{i,average} = \sum_j J_{ij} / n$ where ***n*** is equal to the number of J_{ij} pathways

For **1** and **3** the two different g factors are the following:

$$g_{body} = -\frac{50\, e^{-\frac{4\alpha\lambda}{kT}}(2+\alpha)(J_{bb} + 2J_{Wb})}{81\left(3 + e^{-\frac{4\alpha\lambda}{kT}} + 2e^{-\frac{5\alpha\lambda}{2kT}}\right)\alpha\lambda} + 2\sqrt{\frac{k\,(2\,(\chi_{Mx}.T)_{Co} + (\chi_{Mz}.T)_{Co})}{3N\beta^2}}$$

$$g_{wing} = -\frac{100\, e^{-\frac{4\alpha\lambda}{kT}}(2+\alpha)J_{Wb}}{81\left(3 + e^{-\frac{4\alpha\lambda}{kT}} + 2e^{-\frac{5\alpha\lambda}{2kT}}\right)\alpha\lambda} + 2\sqrt{\frac{k\,(2\,(\chi_{Mx}.T)_{Co} + (\chi_{Mz}.T)_{Co})}{3N\beta^2}}$$

where J_{bb} and J_{wb} are the body-body and wing-body coupling contants respectively.

For **5** there are four different Co(II) ions:

$$g_{Co1} = -\frac{50\, e^{-\frac{4\alpha\lambda}{kT}}\,(j12 + j13 + j14)\,(2+\alpha)}{81\left(3 + e^{-\frac{4\alpha\lambda}{kT}} + 2\,e^{-\frac{5\alpha\lambda}{2kT}}\right)\alpha\lambda} + 2\sqrt{\frac{k\,(2\,(\chi_{Mx}\cdot T)_{Co} + (\chi_{Mz}\cdot T)_{Co})}{3\,N\beta^2}}$$

$$g_{Co2} = -\frac{50\, e^{-\frac{4\alpha\lambda}{kt}}\,(2\,j12 + 2\,j23 + j24)\,(2+\alpha)}{81\left(3 + e^{-\frac{4\alpha\lambda}{kt}} + 2\,e^{-\frac{5\alpha\lambda}{2kt}}\right)\alpha\lambda} + 2\sqrt{\frac{k\,(2\,(\chi_{Mx}\cdot T)_{Co} + (\chi_{Mz}\cdot T)_{Co})}{3\,N\beta^2}}$$

$$g_{Co3} = -\frac{50\, e^{-\frac{4\alpha\lambda}{kT}}\,(j13 + j23)\,(2+\alpha)}{81\left(3 + e^{-\frac{4\alpha\lambda}{kT}} + 2\,e^{-\frac{5\alpha\lambda}{2kT}}\right)\alpha\lambda} + 2\sqrt{\frac{k\,(2\,(\chi_{Mx}\cdot T)_{Co} + (\chi_{Mz}\cdot T)_{Co})}{3\,N\beta^2}}$$

$$g_{Co4} = -\frac{50\, e^{-\frac{4\alpha\lambda}{kT}}\,(2\,j14 + j24)\,(2+\alpha)}{81\left(3 + e^{-\frac{4\alpha\lambda}{kT}} + 2\,e^{-\frac{5\alpha\lambda}{2kT}}\right)\alpha\lambda} + 2\sqrt{\frac{k\,(2\,(\chi_{Mx}\cdot T)_{Co} + (\chi_{Mz}\cdot T)_{Co})}{3\,N\beta^2}}$$

where j_{ij} are the coupling constant between the Co_i and Co_j ions, the other symbols have the same meaning than in the previous formula.

Table S1: BVS calculations for compounds (**1**), (**3**) and (**5**).[1]

(1)		
Atom labels	BVS calculated for Co(II)	BVS calculated for Co(III)
Co(1)	2,0114	2,0554
Co(2)	2,0426	2,0872
(3)		
Atom labels	BVS calculated for Co(II)	BVS calculated for Co(III)
Co(1)	2,0343	2,0787
Co(2)	2,0487	2,0935
(5)		
Atom labels	BVS calculated for Co(II)	BVS calculated for Co(III)
Co(1)	2,0708	2,1161
Co(2)	1,9927	2,0363
Co(3)	2,0040	2,0478
Co(4)	1,9672	2,0102

[1] a) I. D. Brown, D. Altermatt, *Acta Crystallogr.* 1985, **B41**, 244, b) N. E. Brese, M. O'Keeffe, *Acta Crystallogr.* 1991, **B47**, 192, c) M. O'Keeffe, N. E. Brese, *Acta Crystallogr.* 1992, **B48**, 152.