Supporting Information

Polymeric Cobalt(II) Thiolato Complexes – Syntheses, Structures and Properties of $^1_\infty$[Co(SMes)$_2$] and $^1_\infty$[Co(SPh)$_2$NH$_3$].

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List of compounds

`$Co(SPh)_2$´ (**1**)

$^1_\infty[Co(SMes)_2]$ (**2**).

$[Co(SPh)_2(NH_3)_2]$ (**3**).

$^1_\infty[Co(SPh)_2(NH_3)]$ (**4**).

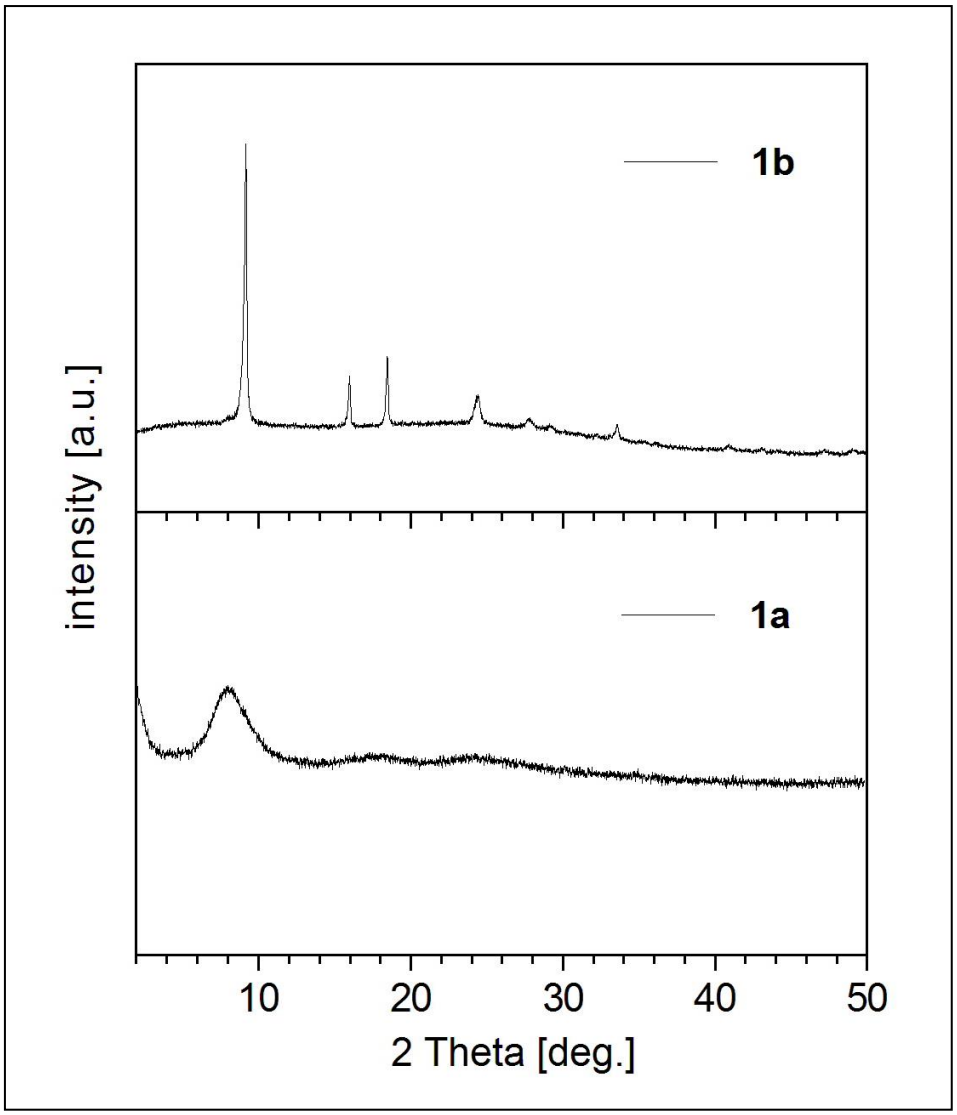

Figure S1 X-ray powder pattern for `$Co(SPh)_2$´ (**1**) synthesized at rt (**1a**) and at 105 °C (**1b**).

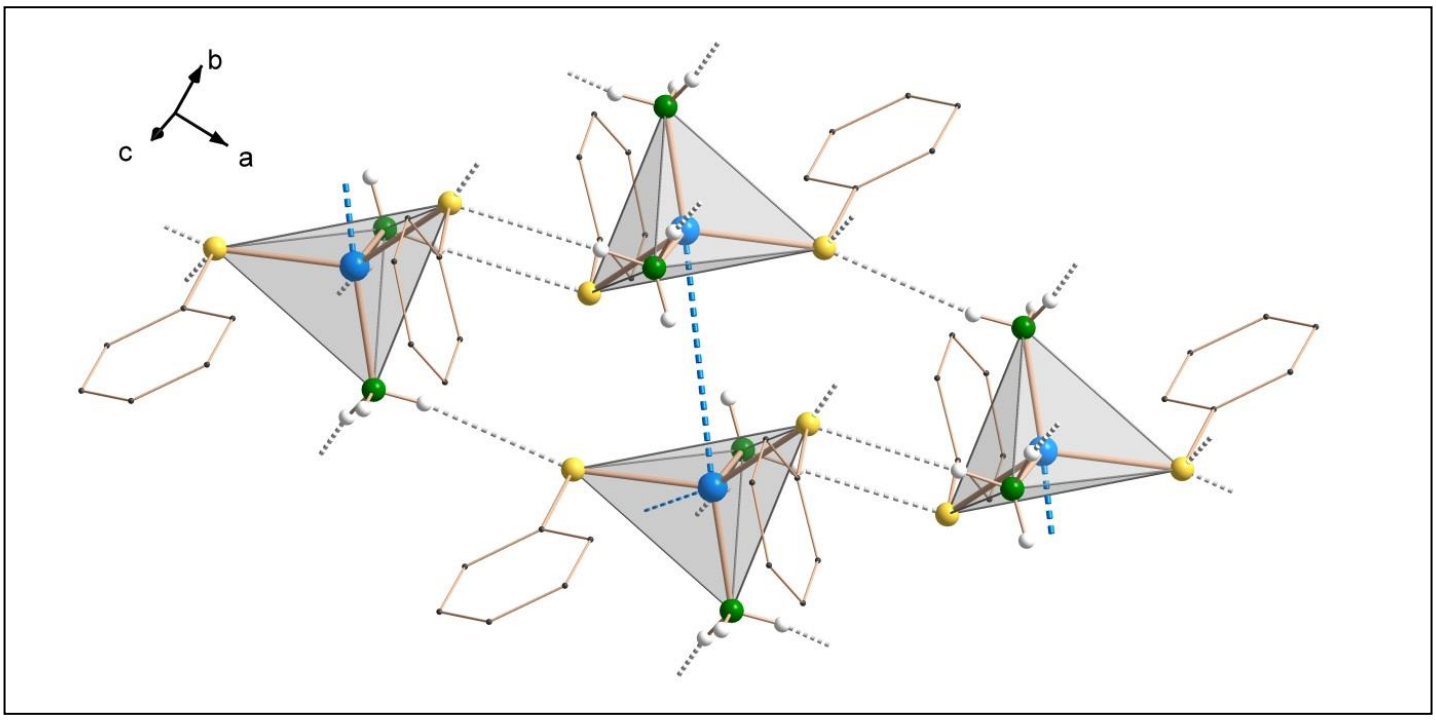

Figure S2 Shortest intermolecular interactions in the crystal structure of $[Co(SPh)_2(NH_3)_2]$ (**3**) (Co: blue, S: yellow, N: green, C: grey, H: white; H atoms of the phenyl rings have been omitted) (Co···Co: pm, S···H pm).

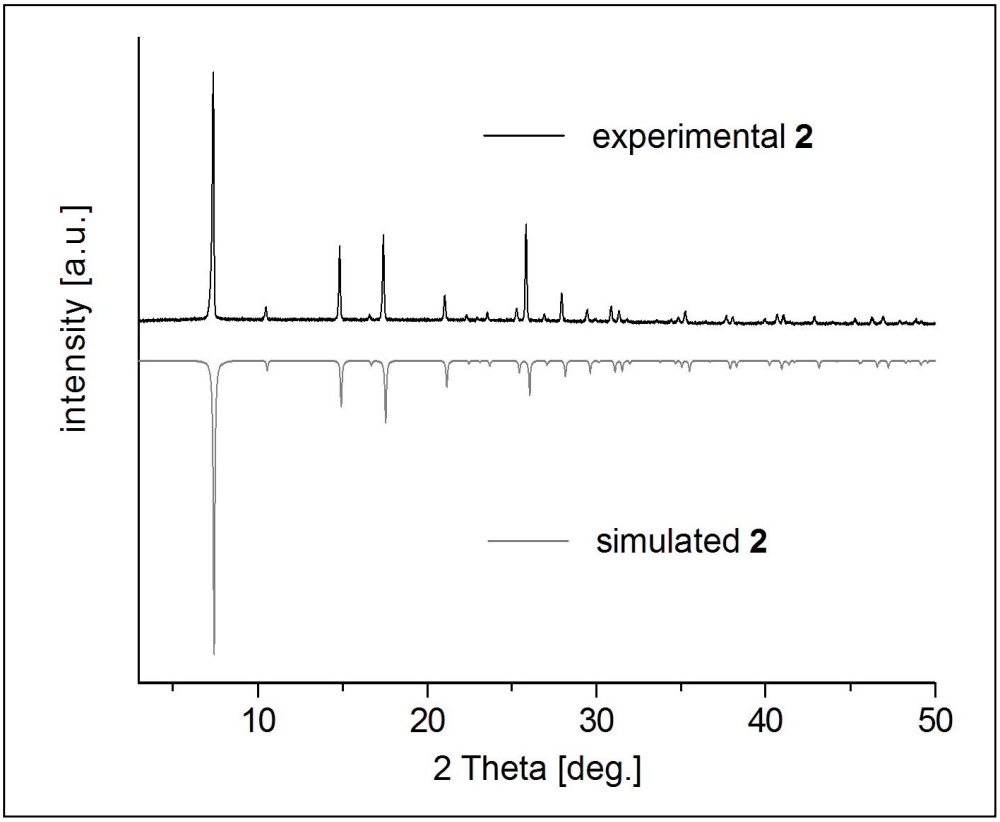

Figure S3 Measured (black) and simulated (grey) X-ray powder patterns for $^{1}_{\infty}[Co(SMes)_2]$.

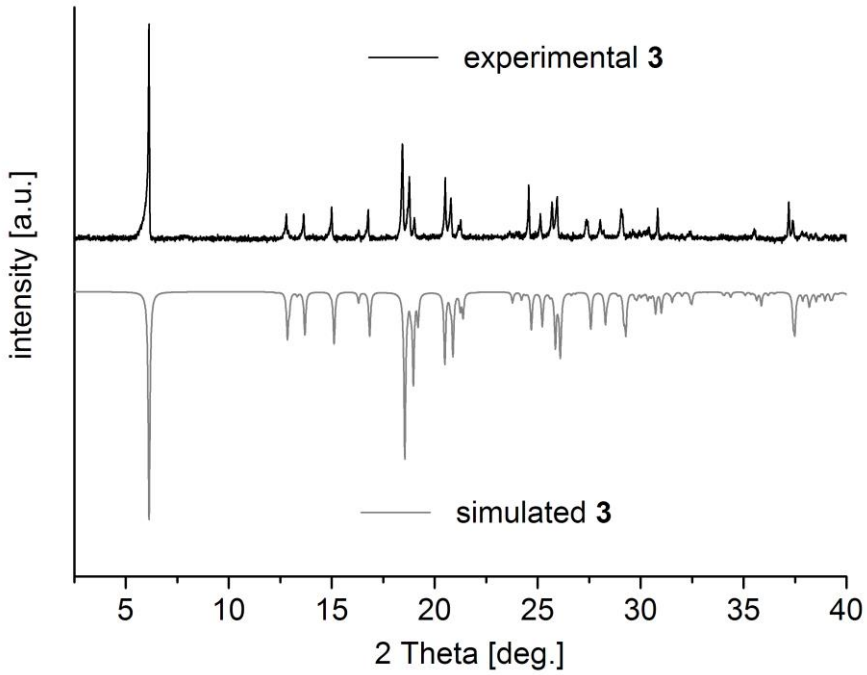

Figure S4 Measured (black) and simulated (grey) X-ray powder patterns for $[Co(SPh)_2(NH_3)_2]$ (**3**).

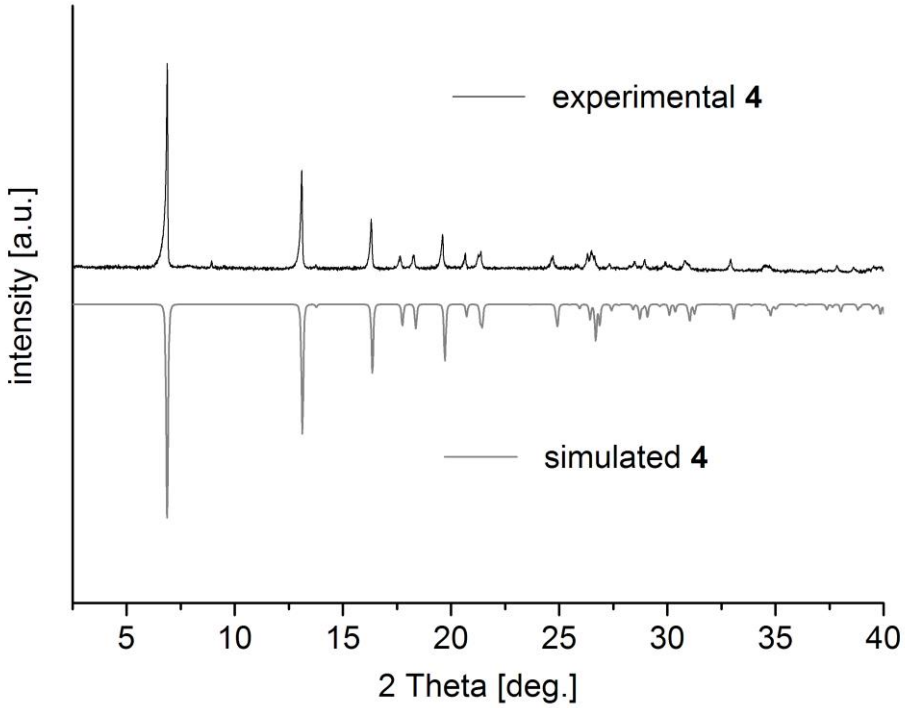

Figure S5 Measured (black) and simulated (grey) X-ray powder patterns for $^{1}_{\infty}[Co(SPh)_2(NH_3)]$ (**4**).

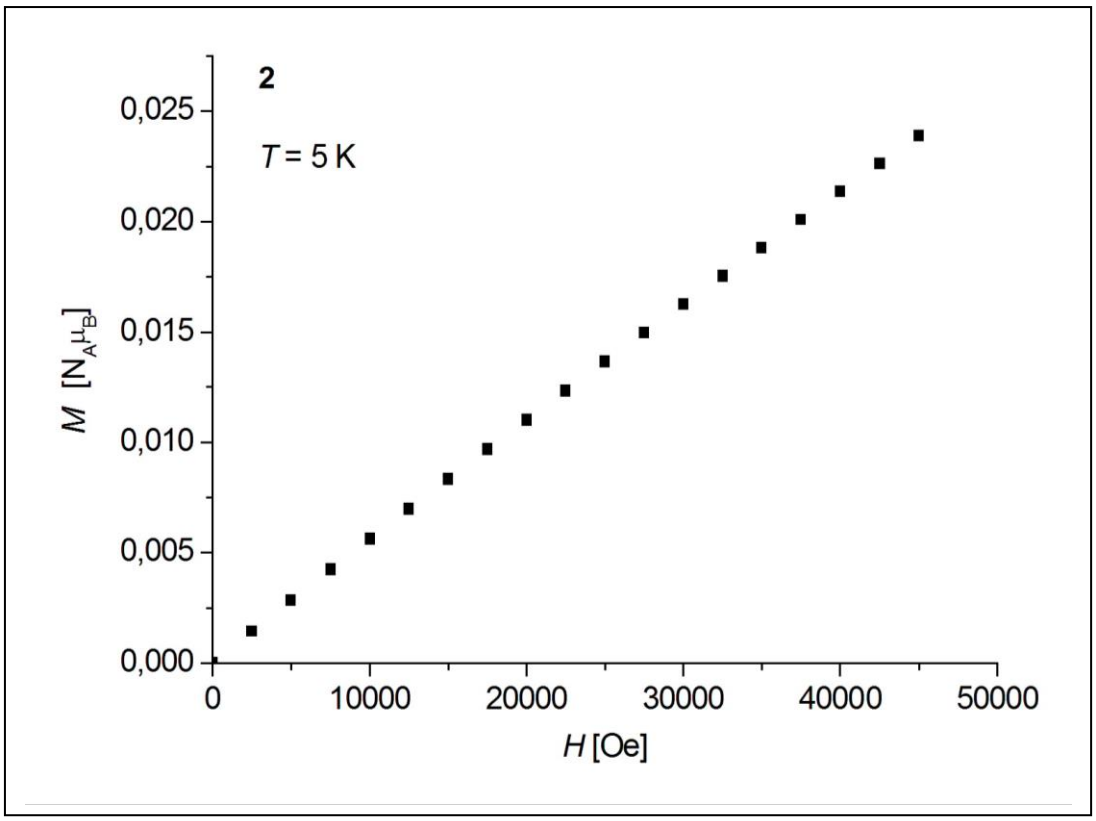

Figure S6 Plot of the magnetization *M* versus *T* for $^{1}_{\infty}$[Co(SMes)$_2$] (**2**) at 5K.

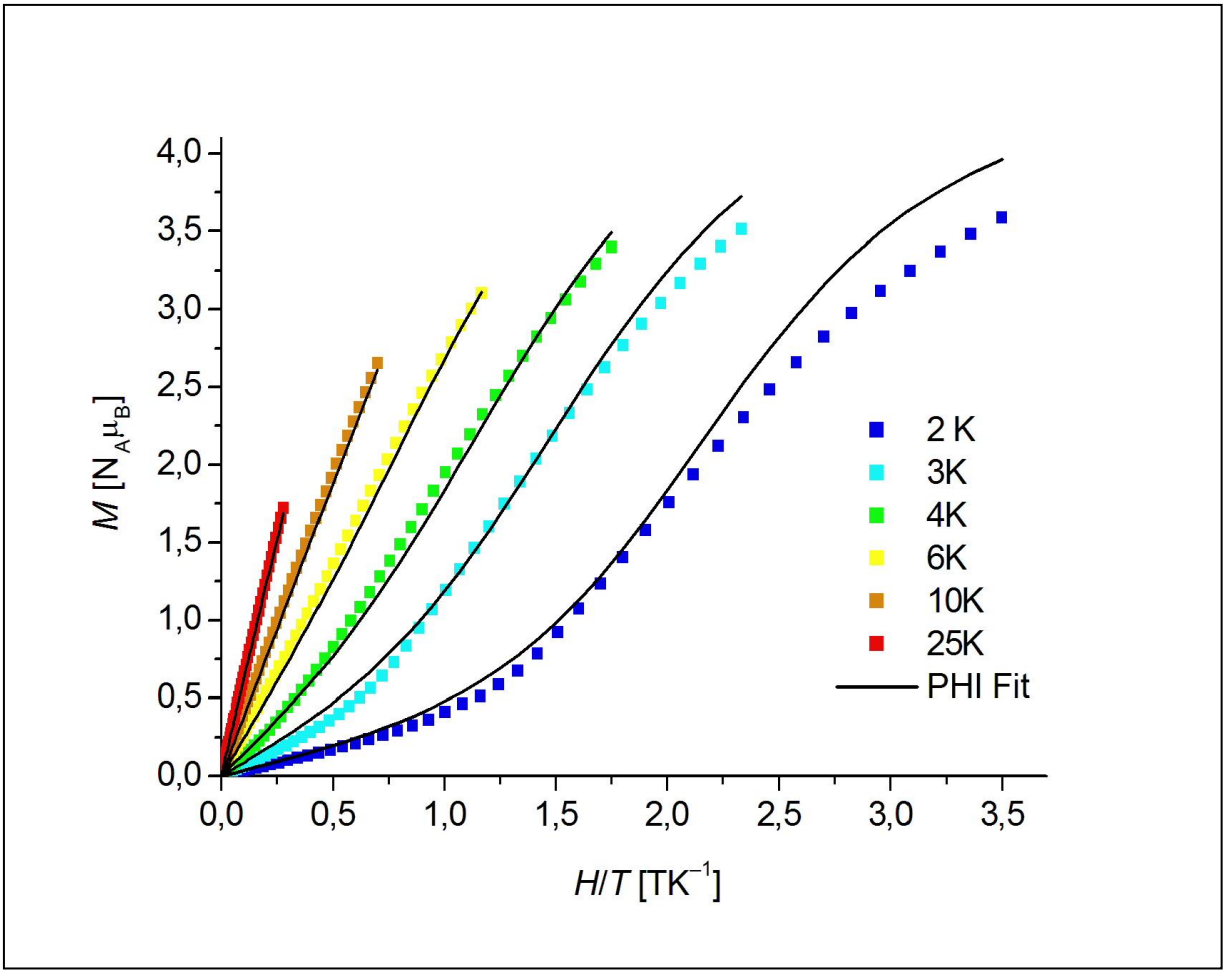

Figure S7 Plots of the reduced magnetization *M* versus *H*/*T* for $[Co(SPh)_2(NH_3)_2]$ (**3**) at different temperatures. The solid lines represent the calculated curves (eqn (1)) with the PHI program.[1]

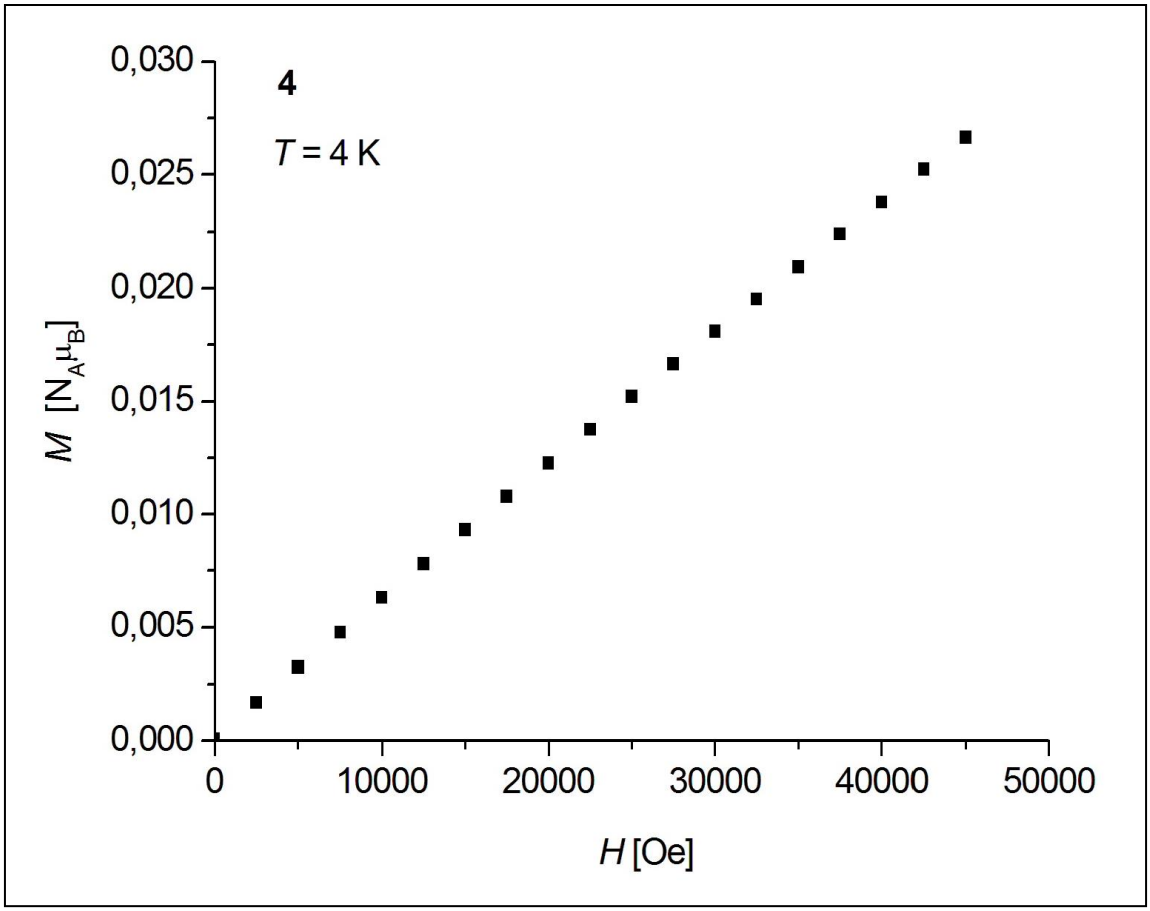

Figure S8 Plot of the magnetization *M* versus *T* for $^{1}_{\infty}[Co(SPh)_2(NH_3)]$ (**4**) at 4K.

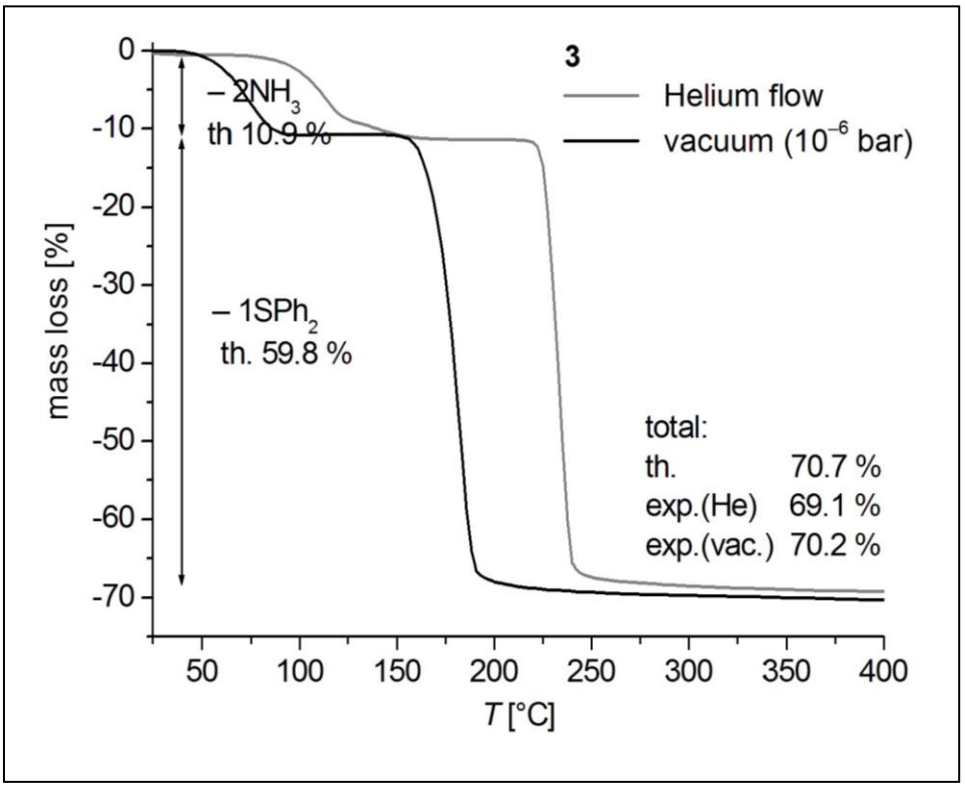

Figure S9 Thermogravimetric analysis of $[Co(SPh)_2(NH_3)_2]$ (**3**) under helium gas flow and in vacuum.

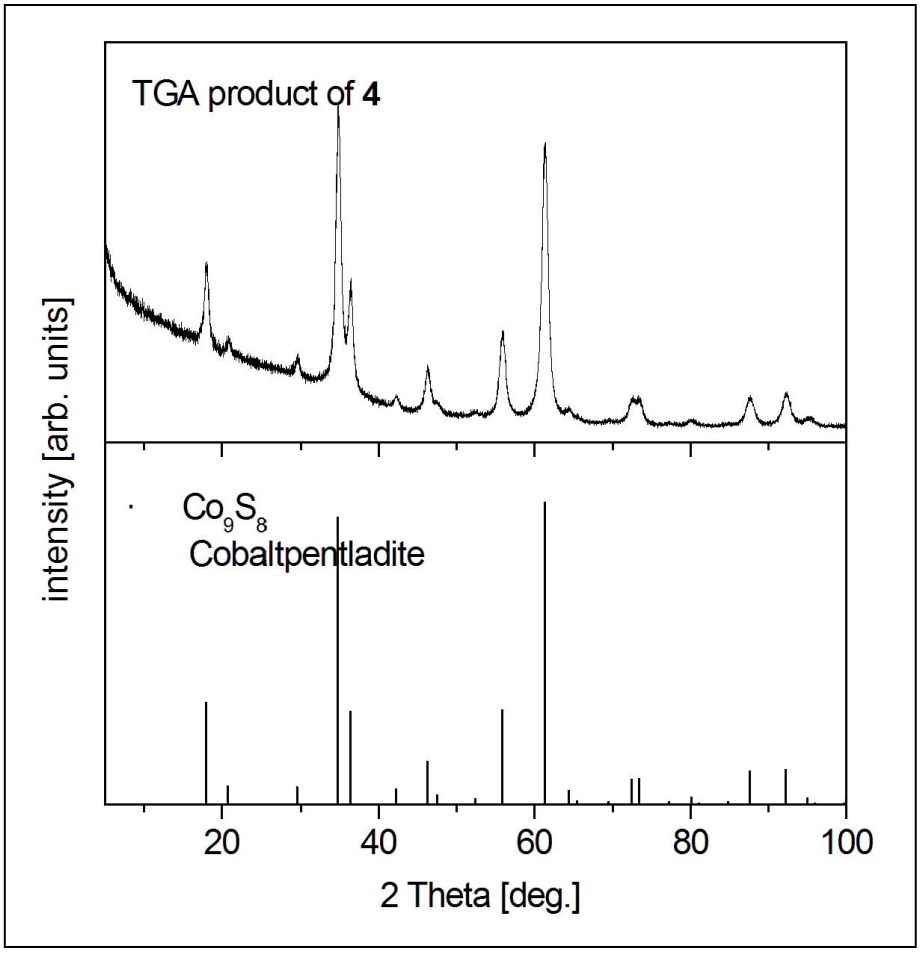

Figure S10 X-ray powder pattern of the vacuum TGA product of $^{1}_{\infty}[Co(SPh)_2(NH_3)]$ (**4**) heated to 555 °C compared to the theoretical peak pattern of the cobalt pentlandite structure from ref (1).

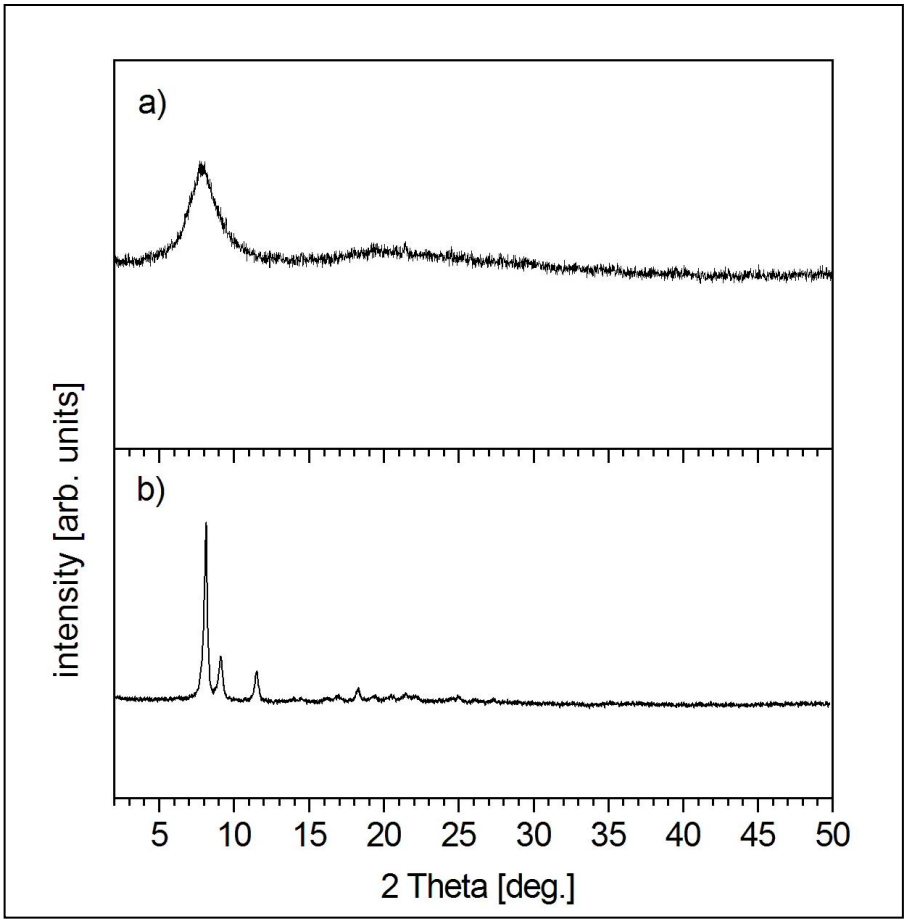

Figure S11 X-ray powder pattern of intermediate TGA products of $^{1}_{\infty}[Co(SPh)_2(NH_3)]$ (**4**) a) heated to 110 °C under vacuum (2K/min) and isothermal treatment for 1 hour b) same residue post-annealed under N_2 at 150 °C for 3 – 4 h..