Supplementary Information for

Engineering solid-state structural transformations and reactions in complexes containing a natural alkaloid for specific switchable properties

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Table S1. Crystallographic data and structure refinement details from single-crystal XRD analysis for [(H-Cn)$CoCl_3$], [(H-Cn)$CoCl_3$]·CH_3OH, [H_2-Cn][$CoCl_4$] and [H_2-Cn][$CoCl_4$]·CH_3CN at 293 K.

Compound	[(H-Cn)$CoCl_3$]	[(H-Cn)$CoCl_3$]·CH_3OH	[H_2-Cn][$CoCl_4$]	[H_2-Cn][$CoCl_4$]·CH_3CN
Crystal colour, habit	blue, stick	blue, prism	blue, block	blue, stick
Empirical formula	$C_{19}H_{23}Cl_3CoN_2O$	$C_{20}H_{27}Cl_3CoN_2O_2$	$C_{19}H_{24}Cl_4CoN_2O$	$C_{21}H_{27}Cl_4CoN_3O$
M_r/g mol^{-1}	460.67	492.71	497.13	538.18
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	8.4143(2)	9.26310(10)	7.02410(10)	8.8394(4)
b/Å	12.7417(2)	12.9486(3)	15.0076(2)	11.8844(7)
c/Å	10.0547(2)	9.3056(2)	21.1727(4)	23.9884(15)
α/°	90	90	90	90
β/°	97.461(2)	93.062(2)	90	90
γ/°	90	90	90	90
V/Å^3	1068.86(4)	1114.56(4)	2231.92(6)	2520.0(2)
Z	2	2	4	4
ρ_{calcd}/g cm^{-3}	1.413	1.468	1.479	1.419
μ/mm^{-1}	9.822	9.491	10.526	9.379
F(000)	474	510	1020	1108
θ range/°	4.435–79.749	4.759–79.518	3.610–77.495	3.685–80.682
Measured reflections	8115	9124	9117	12387
Independent reflections	3235	3890	4004	4903
Observed reflections	3066	3723	3547	3338
No. of parameters, restraints	253, 3	256, 1	249, 1	275, 1
R_{int}	0.0382	0.0262	0.0899	0.0655
R, wR [$I > 2\sigma(I)$]	0.0326, 0.0877	0.0336, 0.0897	0.0364, 0.0879	0.0644, 0.1718
R, wR [all data]	0.0344, 0.0886	0.0351, 0.0906	0.0429, 0.0909	0.0897, 0.1966
Goodness of fit	1.035	1.044	1.059	1.031
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	0.341, -0.334	0.306, -0.209	0.385, -0.205	0.529, -0.794
Flack parameter	-0.014(4)	-0.023(3)	-0.036(3)	-0.035(8)

Table S2. Crystallographic data and structure refinement details from PXRD analysis for compounds $[(H\text{-}Cn)CoCl_3]\cdot H_2O$, $[H_2\text{-}Cn][CoCl_4]\cdot CH_3OH$ and $[H_2\text{-}Cn][CoCl_4]\cdot H_2O$ at 293 K.

Compound	$[(H\text{-}Cn)CoCl_3]\cdot H_2O$	$[H_2\text{-}Cn][CoCl_4]\cdot CH_3OH$	$[H_2\text{-}Cn][CoCl_4]\cdot H_2O$
Empirical formula	$C_{19}H_{25}Cl_3CoN_2O_2$	$C_{20}H_{28}Cl_4CoN_2O_2$	$C_{19}H_{26}Cl_4CoN_2O_2$
M_r/g mol^{-1}	478.70	529.19	515.16
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	8.573	32.585	25.604
b/Å	13.051	8.865	13.371
c/Å	9.916	8.234	12.663
α/°	90	90	90
β/°	96.94	90	90
γ/°	90	90	90
V/Å^3	1101.43	2378.81	4335.63
Z	2	4	4
Step size/°	0.013	0.013	0.013
2θ range/°	4–50	4–50	4–50
R_p	0.0253	0.0230	0.0255
R_{wp}	0.0319	0.0293	0.0321
R_{exp}	0.0308	0.0331	0.0295
Background	Chebyshev polynomial of 6th order		

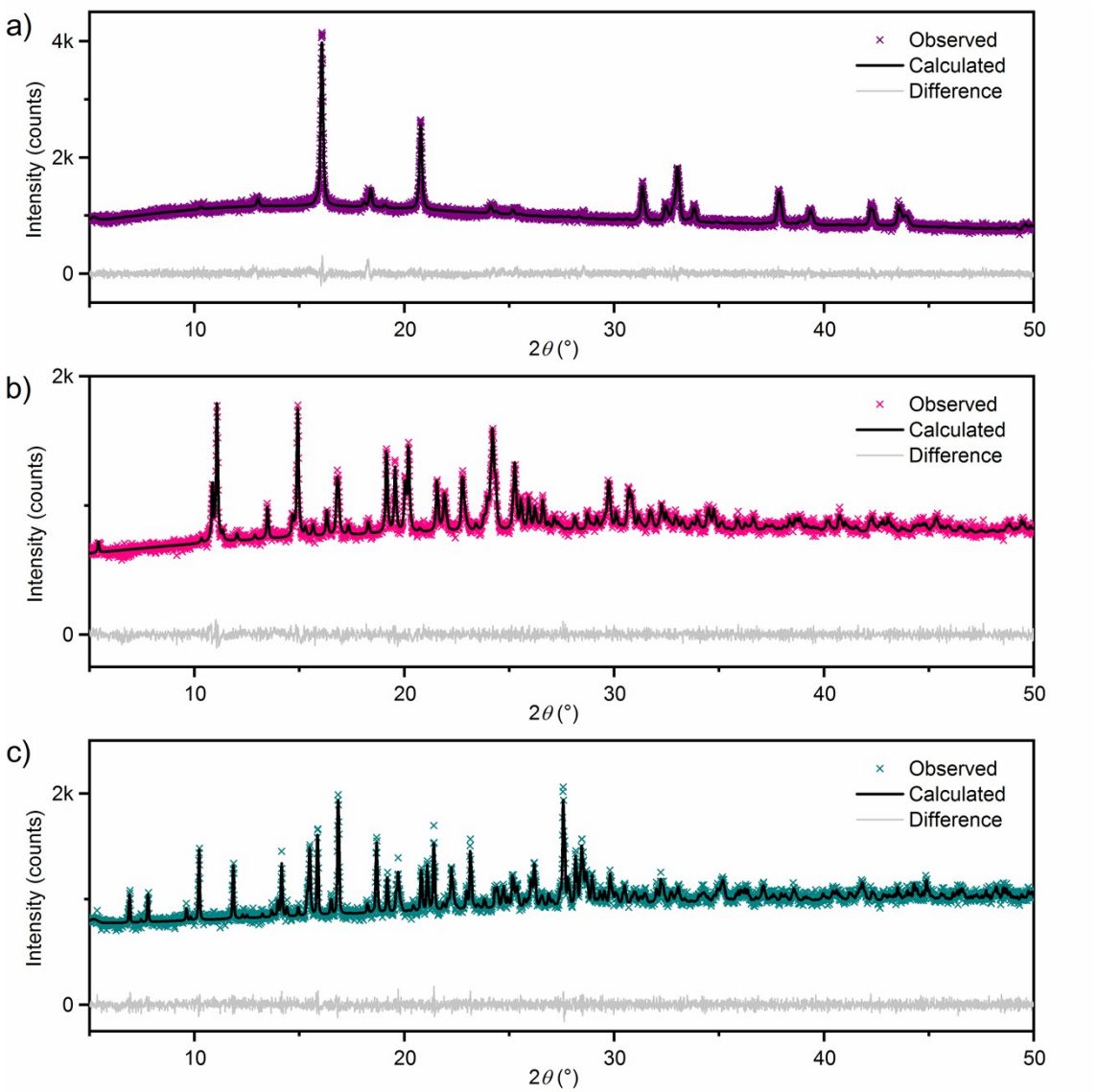

Figure S1. PXRD pattern and profile fitting results for a) $[(H\text{-}Cn)CoCl_3]\cdot H_2O$, b) $[H_2\text{-}Cn][CoCl_4]\cdot CH_3OH$ and c) $[H_2\text{-}Cn][CoCl_4]\cdot H_2O$ at 293 K.

Table S3. Selected bond lengths (Å) and angles (°) of the cobalt(II) coordination sphere in compounds [(H-Cn)$CoCl_3$], [(H-Cn)$CoCl_3$]·CH_3OH, [H_2-Cn][$CoCl_4$] and [H_2-Cn][$CoCl_4$]·CH_3CN.

	[(H-Cn)$CoCl_3$]	[(H-Cn)$CoCl_3$]·CH_3OH	[H_2-Cn][$CoCl_4$]	[H_2-Cn][$CoCl_4$]·CH_3CN
Co1–Cl1	2.254(1)	2.243(1)	2.283(1)	2.271(2)
Co1–Cl2	2.296(1)	2.281(1)	2.257(1)	2.266(3)
Co1–Cl3	2.234(1)	2.252(1)	2.295(1)	2.275(2)
Co1–N1	2.057(2)	2.071(3)	-	-
Co1–Cl4	-	-	2.254(1)	2.263(4)
Cl1–Co1–Cl2	103.19(4)	115.44(5)	110.47(5)	112.96(10)
Cl1–Co1–Cl3	115.96(5)	112.00(5)	108.76(5)	108.02(10)
Cl1–Co1–N1	111.83(10)	105.98(8)	-	-
Cl1–Co1–Cl4	-	-	109.56(5)	112.91(11)
Cl2–Co1–Cl3	115.84(6)	106.03(4)	107.73(5)	103.95(9)
Cl2–Co1–N1	103.26(10)	106.45(11)	-	-
Cl2–Co1–Cl4	-	-	112.60(5)	108.71(12)
Cl3–Co1–N1	106.18(8)	110.84(11)	-	-
Cl3–Co1–Cl4	-	-	107.59(5)	109.90(11)
CShM[a]	0.5776	0.3457	0.0281	0.1109

[a]Pinsky M, Avnir D (1998) Continuous symmetry measures. 5. The classical polyhedra. Inorganic Chemistry 37: 5575-5582.

Table S4. Analysis of short ring-interactions with Cg(*i*)···Cg(*j*) distances < 6.0 Å and $\beta < 60.0°$ for compounds [(H-Cn)$CoCl_3$], [(H-Cn)$CoCl_3$]·CH_3OH, [H_2-Cn][$CoCl_4$] and [H_2-Cn][$CoCl_4$]·CH_3CN.

Compound	Cg(*i*)···Cg(*j*)	Cg(*i*)···Cg(*j*)/Å[a]	α/°[b]	β/°[c]	Cg(*i*)···plane [Cg(*j*)]/Å[d]	Symmetry operator
[(H-Cn)$CoCl_3$]	(N1→C9)···(C4→C9)	5.090(2)	57.77	27.3	0.4470(15)	1 – *x*, 1/2 – *y*, 1 – *z*
[(H-Cn)$CoCl_3$]·CH_3OH	(N1→C9)···(C4→C9)	5.183(2)	40.73	33.8	1.3804(14)	1 – *x*, –1/2 + *y*, 1 – *z*
[H_2-Cn][$CoCl_4$]	(N1→C9)···(C4→C9)	5.183(3)	2.1	45.0	3.5361(18)	–1 + *x*, *y*, *z*
	(C4→C9)···(N1→C9)	5.182(3)	2.1	47.0	3.6627(18)	1 + *x*, *y*, *z*
[H_2-Cn][$CoCl_4$]·CH_3CN	(N1→C9)···(C4→C9)	5.944(6)	25.1	44.5	2.617(4)	1 – *x*, –1/2 + *y*, 1/2 –*z*
	(C4→C9)···(N1→C9)	5.609(6)	25.1	46.5	2.256(4)	–*x*, 1/2 + *y*, 1/2 – *z*

[a] Cg = centre of gravity of the aromatic ring. [b] α = angle between the planes of two aromatic rings. [c] β = angle between the Cg···Cg line and the normal to the plane of the first aromatic ring.

Table S5. Analysis of C–H···Cg and Y–X···Cg (π-ring) interactions (H···Cg(*j*) < 3.0 Å or X···Cg(*j*) < 4.0 Å; and $\gamma < 30.0°$) for compounds [(H-Cn)$CoCl_3$], [(H-Cn)$CoCl_3$]·CH_3OH, [H_2-Cn][$CoCl_4$] and [H_2-Cn][$CoCl_4$]·CH_3CN.

Compound	C–H···Cg(*j*)	H···Cg(*j*)/Å[a]	γ/°[b]	C–H···Cg(*j*)/°[c]	C···Cg(*j*)/Å	C–H, π /°[d]	Symmetry operator
[(H-Cn)$CoCl_3$]	C13–H13···(C4→C9)	2.75	12.74	151	3.643(5)	61	1 + *x*, *y*, *z*
	C19A–H19A···(N1→C9)	2.80	12.05	160	3.69(2)	59	1 + x, y, z
[(H-Cn)$CoCl_3$]·CH_3OH	C14–H14B···(N1→C9)	2.93	13.34	134	3.670(5)	51	*x*, *y*, 1 + *z*
	C20–H20B···(C4→C9)	2.86	21.62	151	3.728(8)	64	–1 + *x*, *y*, *z*
Compound	**Y–X···Cg(*j*)**	**X···Cg(*j*)/Å[a]**	**γ/°[c]**	**Y–X···Cg(*j*)/°[d]**	**Y···Cg(*j*)/Å**	**Y–X, π /°[d]**	**Symmetry operator**
[H_2-Cn][$CoCl_4$]	Co1–Cl1···(N1→C9)	3.546(2)	19.07	109	4.802(1)	38	–1/2 + *x*, 1/2 – *y*, 1 – *z*
	Co1–Cl1···(C4→C9)	3.549(2)	19.09	148	5.6254(1)	40	–1/2 + *x*, 1/2 – *y*, 1 – *z*
[H_2-Cn][$CoCl_4$]·CH_3CN	Co1–Cl4···(N1→C9)	3.826(4)	23.34	113	5.147(4)	34	–*x*, –1/2 + *y*, 1/2 – *z*

[a] Cg(*j*) = centre of gravity of the aromatic (π) ring. [b] γ = angle between Cg(*j*)–H vector and ring Cg(*j*) normal. [c] γ = angle between Cg(*j*)–X vector and ring Cg(*j*) normal. [d] = angle of the C–H or Y–X bond with the π -plane (i.e. Perpendicular = 90°, Parallel = 0°).

Table S6. Hydrogen-bonding geometry in compounds [(H-Cn)$CoCl_3$], [(H-Cn)$CoCl_3$]·CH_3OH, [H_2-Cn][$CoCl_4$] and [H_2-Cn][$CoCl_4$]·CH_3CN.

Compound	*D*–H···*A*	*D*–H/Å	H···*A*/Å	*D*···*A*/Å	*D*–H···*A*/°	Symm. op. on *A*	
[(H-Cn)$CoCl_3$]	O1–H1O···Cl2	0.82	2.53	3.243(3)	145	*x*, *y*, –1 + *z*	
	N2–H2N···Cl1	0.98	2.60	3.338(3)	132	*x*, *y*, –1 + *z*	
	N2–H2N···Cl2	0.98	2.69	3.484(3)	138	*x*, *y*, –1 + *z*	
	C1–H1···Cl2	0.93	2.68	3.364(4)	130	*x*, *y*, *z*	intra
	C2–H2···O1	0.93	2.26	2.626(5)	103	*x*, *y*, *z*	intra
	C15–H15A···Cl2	0.97	2.80	3.646(5)	146	1 – *x*, 1/2 + *y*, 1 – *z*	
	C16–H16B···O1	0.97	2.32	2.998(6)	126	*x*, *y*, *z*	intra
[(H-Cn)$CoCl_3$]·CH_3OH	O1–H1O···Cl2	0.82	2.48	3.280(3)	167	1 – *x*, *y*, *z*	
	N2–H2N···O2	0.98	1.80	2.756(5)	165	*x*, *y*, *z*	
	O2–H2O···Cl3	0.82	2.45	3.194(4)	152	1 – *x*, *y*, *z*	intra
	C2–H2···O1	0.93	2.41	2.745(5)	101	*x*, *y*, *z*	
	C15–H15A···Cl2	0.97	2.79	3.643(5)	148	*1* – *x*, –1/2 + *y*, 1 – *z*	
	C16–H16A···Cl1	0.97	2.80	3.680(4)	151	–1 + *x*, *y*, 1 + *z*	intra
	C16–H16B···O1	0.97	2.29	2.959(5)	125	*x*, *y*, *z*	
[H_2-Cn][$CoCl_4$]	N1–H1N···Cl1	0.99	2.20	3.162(4)	165	*x*, *y*, *z*	
	O1–H1O···Cl3	0.82	2.44	3.212(3)	157	1/2 – *x*,1 – *y*,–1/2 + *z*	
	N2–H2N···Cl3	0.98	2.40	3.234(4)	142	3/2 – *x*,1 – *y*, –1/2 + *z*	
	C1–H1···Cl1	0.93	2.79	3.640(6)	152	–1/2 + *x*,1/2 – *y*,1 – *z*	
	C2–H2···O1	0.93	2.41	2.750(6)	101	*x*, *y*, *z*	intra
	C5–H5···.Cl3	0.93	2.73	3.628(5)	162	3/2 – *x*,1 – *y*, –1/2 + *z*	
	C7–H7···Cl4	0.93	2.73	3.591(5)	154	1 + *x*, *y*, *z*	
	C12–H12B···O1	0.97	2.38	2.841(6)	109	*x*, *y*, *z*	intra
	C15–H15B···O1	0.97	2.42	3.092(6)	126	*x*, *y*, *z*	intra
	C16–H16A···O1	0.97	2.47	3.348(7)	151	1 + *x*, *y*, *z*	
	C16–H16B···Cl4	0.97	2.81	3.581(6)	137	3/2 – *x*,1 – *y*, –1/2 + *z*	
[H_2-Cn][$CoCl_4$]·CH_3CN	N1–H1N···Cl1	0.86	2.35	3.177(8)	163	*x*, *y*, *z*	
	O1–H1O···Cl4	0.85	2.59	3.333(7)	147	1 – *x*, 1/2 + *y*, 1/2 + *z*	
	N2–H2N···Cl2	0.98	2.38	3.210(6)	142	1 – *x*, 1/2 + *y*, 1/2 + *z*	
	N2–H2N···Cl3	0.98	2.80	3.494(7)	129	1 – *x*, 1/2 + *y*, 1/2 + *z*	
	C2–H2···O1	0.93	2.39	2.752(11)	103	*x*, *y*, *z*	intra
	C5–H5···Cl3	0.93	2.78	3.706(10)	173	1 – *x*, 1/2 + *y*, 1/2 + *z*	
	C10–H10···Cl3	0.98	2.79	3.609(8)	142	1 – *x*, 1/2 + *y*, 1/2 + *z*	
	C15–H15B···O1	0.97	2.36	3.020(12)	125	*x*, *y*, *z*	intra

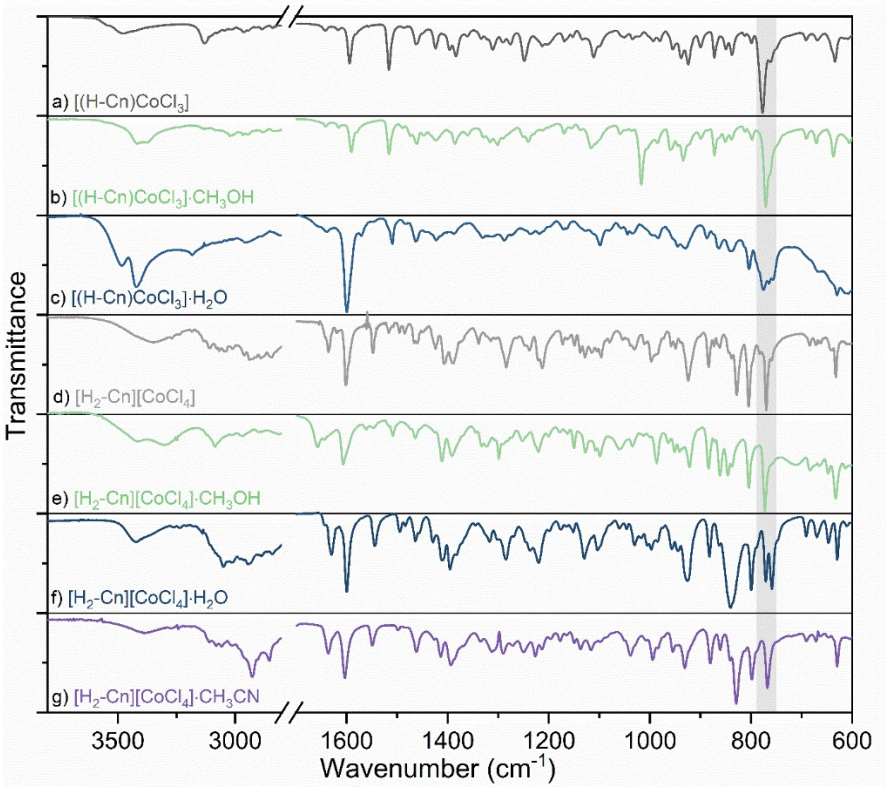

Figure S2. ATR-FTIR spectra of prepared cinchonine-chloro-cobalt(II) compounds.

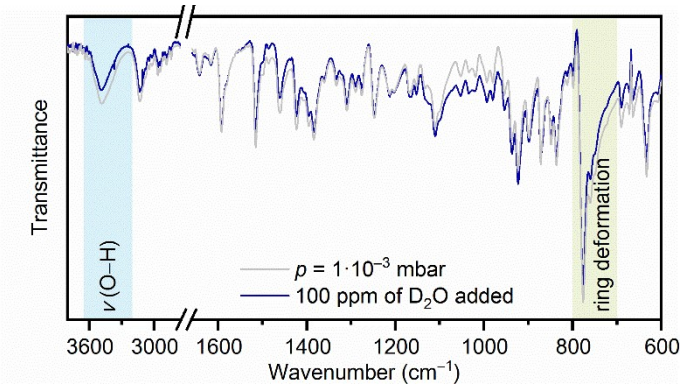

Figure S3. Vacuum FTIR observation of structural transformation in the solvent-free phase [(H-Cn)$CoCl_3$] during exposure and subsequent removal of D_2O.

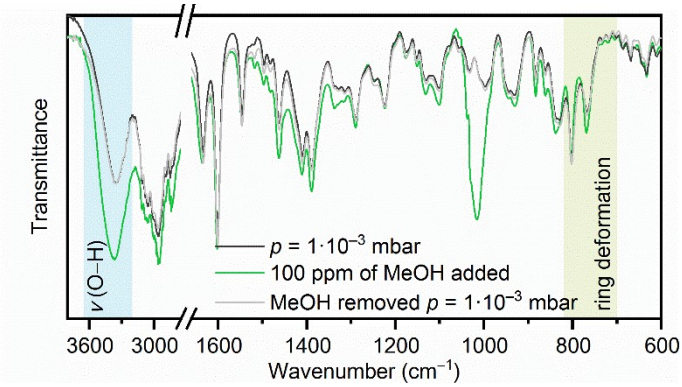

Figure S4. Vacuum FTIR observation of structural transformation in the solvent-free phase [H_2-Cn][$CoCl_4$] during exposure and subsequent removal of methanol.

Table S7. Thermogravimetric analysis of prepared cinchonine-chloro-cobalt(II) compounds.

Compound	*w* (solvent) / %		*w* (CoO, residue) / %	
	calculated	experimental	calculated	experimental
[(H-Cn)$CoCl_3$]	-	-	16.26	16.69
[(H-Cn)$CoCl_3$]·CH_3OH	6.50	5.57 (340 – 400 K)	15.20	15.52
[(H-Cn)$CoCl_3$]·H_2O	3.76	3.92 (300 – 337 K)	15.65	15.57
[H_2-Cn][$CoCl_4$]·CH_3OH	6.05	5.60 (340 – 400 K)	14.14	14.72
[H_2-Cn][$CoCl_4$]·H_2O	3.49	2.03 (310 – 398 K)	14.54	14.51
[H_2-Cn][$CoCl_4$]·CH_3CN	7.63	6.71 (323 – 410 K)	13.92	13.42

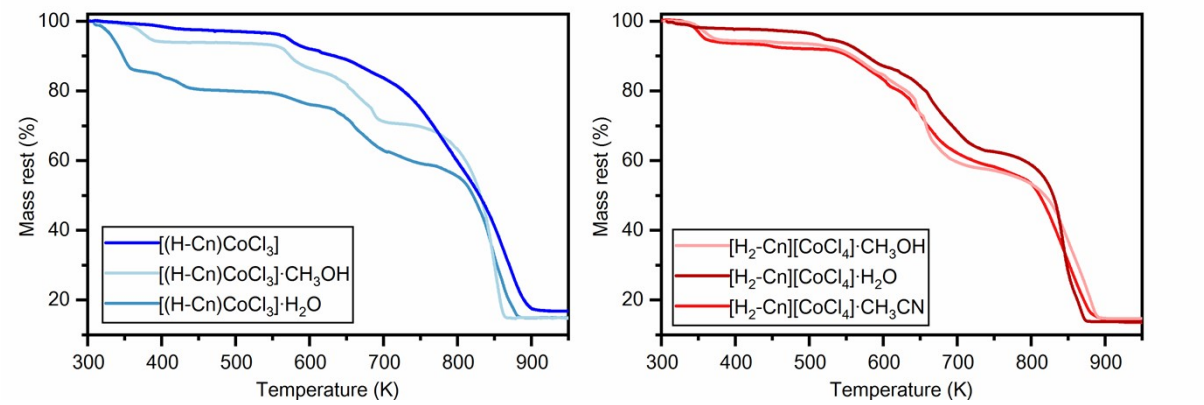

Figure S5. TG curves for decomposition of prepared cinchonine-chloro-cobalt(II) compounds.