

**Slow magnetic relaxation behaviour of tetrahedrally coordinated Co<sup>2+</sup> in imidazo[1,5-*a*]pyridinium-based (C<sub>13</sub>H<sub>12</sub>N<sub>3</sub>)<sub>2</sub>[CoCl<sub>4</sub>] hybrid salt and [Co(C<sub>13</sub>H<sub>12</sub>N<sub>3</sub>)Cl<sub>3</sub>] molecular complex**

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**Supplementary data**

**Table S1.** Selected bond lengths [Å] and angles [°] for [L]<sub>2</sub>[CoCl<sub>4</sub>] (**1**) and [CoLCl<sub>3</sub>] (**2**).

<b>1</b>		<b>2</b>	
Co(1)–Cl(4)	2.2619(5)	Co(1)–N(132)	2.0767(19)
Co(1)–Cl(2)	2.2682(5)	Co(1)–Cl(2)	2.2370(6)
Co(1)–Cl(1)	2.2843(5)	Co(1)–Cl(3)	2.2480(6)
Co(1)–Cl(3)	2.2977(5)	Co(1)–Cl(1)	2.2582(6)
Cl(4)–Co(1)–Cl(2)	109.294(19)	N(132)–Co(1)–Cl(2)	114.94(5)
Cl(4)–Co(1)–Cl(1)	106.938(18)	N(132)–Co(1)–Cl(3)	100.63(5)
Cl(2)–Co(1)–Cl(1)	110.329(17)	Cl(2)–Co(1)–Cl(3)	109.84(2)
Cl(4)–Co(1)–Cl(3)	112.667(18)	N(132)–Co(1)–Cl(1)	100.45(5)
Cl(2)–Co(1)–Cl(3)	111.342(18)	Cl(2)–Co(1)–Cl(1)	112.28(2)
Cl(1)–Co(1)–Cl(3)	106.135(18)	Cl(3)–Co(1)–Cl(1)	118.01(3)
C(11)–N(12)	1.366(2)	C(11)–N(12)	1.362(3)
C(11)–C(17a)	1.373(2)	C(11)–C(17a)	1.374(3)
N(12)–C(13)	1.346(2)	N(12)–C(13)	1.337(3)
N(12)–C(12)	1.469(2)	N(12)–C(12)	1.468(3)
C(13)–N(13a)	1.362(2)	C(13)–N(13a)	1.348(3)
C(13)–C(131)	1.462(2)	C(13)–C(131)	1.485(3)
N(13a)–C(14)	1.397(2)	N(13a)–C(14)	1.391(3)
N(13a)–C(17a)	1.402(2)	N(13a)–C(17a)	1.402(3)
C(17)–C(17a)	1.414(2)	C(17)–C(17a)	1.415(3)
C(21)–N(22)	1.361(2)		
C(21)–C(27a)	1.375(2)		
N(22)–C(23)	1.354(2)		
N(22)–C(22)	1.465(2)		
C(23)–N(23a)	1.359(2)		
C(23)–C(231)	1.464(2)		
N(23a)–C(24)	1.395(2)		
N(23a)–C(27a)	1.406(2)		
C(27)–C(27a)	1.417(2)		

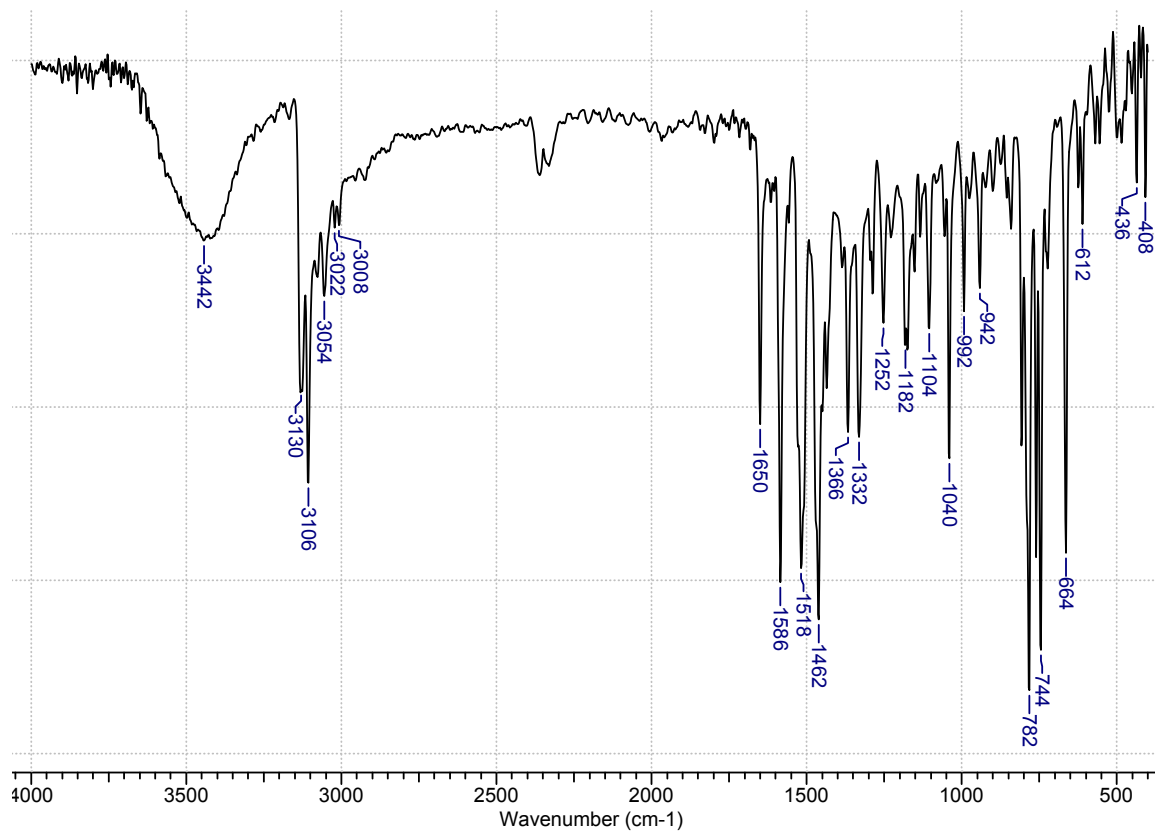


Figure S1. IR spectrum of  $[L]_2[CoCl_4]$  (1).

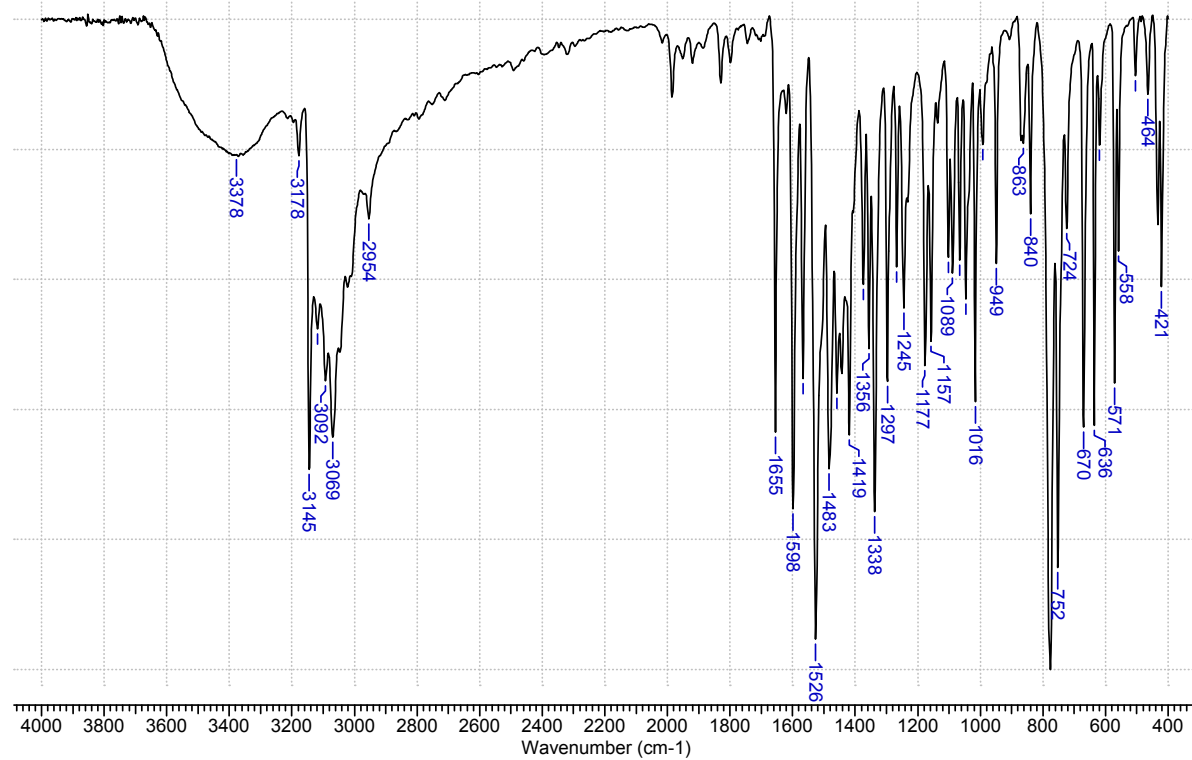
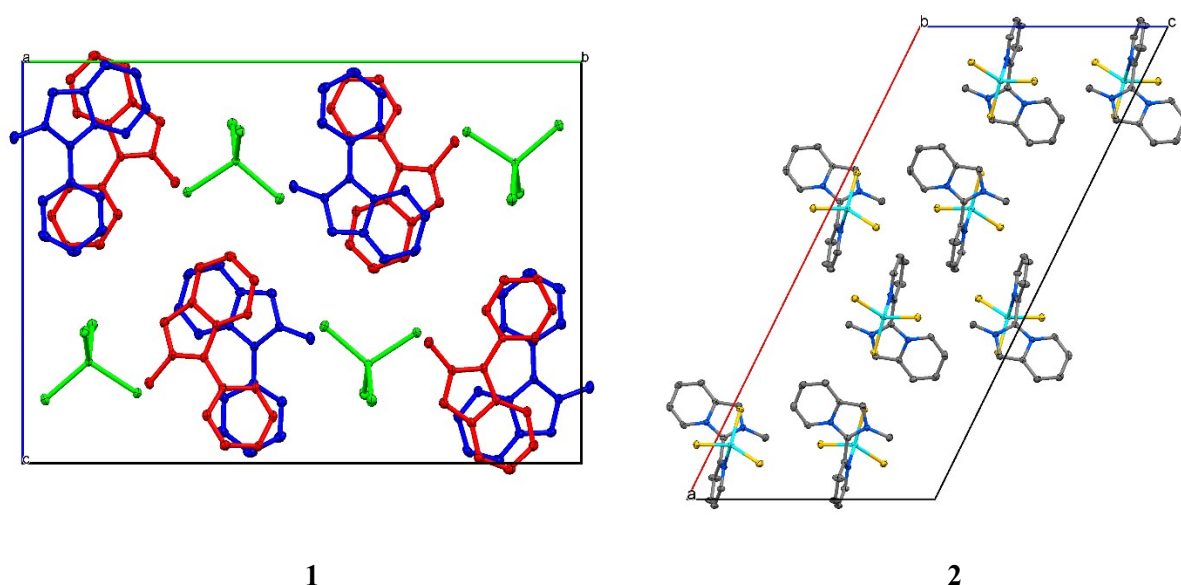


Figure S2. IR spectrum of  $[CoCl_3]$  (2).



**Figure S3.** Fragments of crystal packing of  $[L]_2[CoCl_4]$  (**1**) and  $[CoCl_3]$  (**2**) viewed along  $a$  and  $b$  directions, respectively. L1 and L2 cations in **1** are shown in red and blue. H-atoms are omitted for clarity.

### Ab initio calculations

*Ab initio* calculations were performed with ORCA 4.0.0 computational package [1] using the experimental geometries of  $[CoCl_4]^{2-}$  and  $[CoCl_3]$ . The relativistic effects were included in the calculations with zero-order regular approximation (ZORA) together with the scalar relativistic contracted version of def2-TZVP basis functions for all elements. The calculations of ZFS parameters were based on state average complete active space self-consistent field (SA-CASSCF) wave functions complemented by N-electron valence second order perturbation theory (NEVPT2) [2]. The active space of the CASSCF calculations comprised of seven electrons in five metal-based d-orbitals. The state averaged approach was used, in which all 10 quartet and 40 doublet states were equally weighted. The calculations utilized the RI approximation with appropriate decontracted auxiliary basis set and the chain-of-spheres (RIJCOSX) approximation to exact exchange. Increased integration grids (Grid5 and GridX6) and tight SCF convergence criteria were used. The ZFS parameters were calculated through quasi-degenerate perturbation theory in which an approximation to the Breit-Pauli form of the spin-orbit coupling operator (SOMF) and the effective Hamiltonian theory was utilized [3].

The calculated energies of multielectron terms for **1** are 0 for the ground term  $^4A_2$ , {3188, 3344, 3617} for three members arising from the mother term  $^4T_2$ , {5682, 6019, 6182} for  $^4T_1$ , and {18400, 18442, 18654} for  $^2^4T_1$  (Table S2). The ground term  $^4A_2$  is split due to spin-orbit coupling to multiplets (Kramers doublets) separated by  $\delta = 8.1 \text{ cm}^{-1}$ . This gap is recovered by the traditional zero-field splitting parameters  $D = 3.96 \text{ cm}^{-1}$  and  $E/D = 0.12$ , respectively,  $\delta = 2(D^2 + 3E^2)^{1/2}$ . Three  $g$ -factors are {2.314, 2.355, 2.367} which points to only a slight magnetic anisotropy. These magnetic parameters need to be accepted by care since the calculations refer to an insulated anionic fragment of the solid-state compound. A more detailed view to the individual contributions to the  $D$  and  $E$  parameter for **1** show that only the first three excitation energies contribute substantially: +15.2, +14.3 and  $-25.4 \text{ cm}^{-1}$  for  $D$ , and +15.9,  $-14.6$ , and  $-0.89 \text{ cm}^{-1}$  for  $E$  (Table S3).

For complex  $[CoCl_3]$  (**2**), the *ab initio* calculations also confirmed the orbitally nondegenerate ground state. The main results are collected in Table S2. The calculated ZFS  $D$ -parameter is relatively large and positive ( $D = 19.8 \text{ cm}^{-1}$ ) with a moderate rhombic component ( $E/D = 0.17$ ). Individual contributions to the total  $D$  are shown in Table S3. As expected, also in this case the largest contributions originate from three

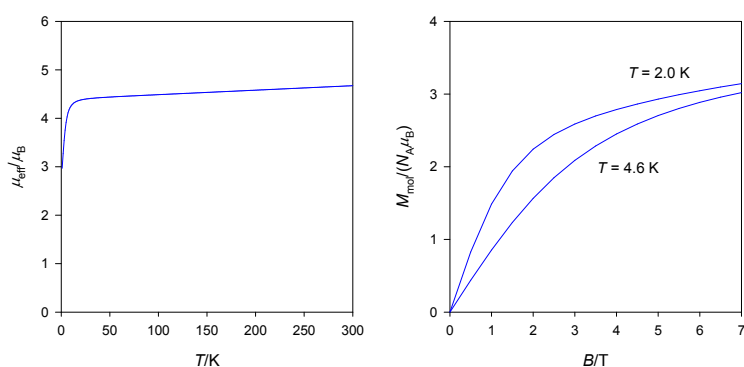
lowest-lying terms ( ${}^4T_2$  term in  $T_d$  symmetry). Unlike the previous complex, these contributions are small, however, all positive. Their summation then results to the large  $D$  value. Calculated  $D$  and  $g$  values are in very good agreement with the experiment.

Magnetic functions (the temperature dependence of the effective magnetic moment and field dependence of magnetization) for **1** have also been calculated whose behaviour corresponds to the experiment (Fig. S4).

**Table S2.** Calculated (CASSCF/NEVPT2) energies and magnetic parameters for  $[L]_2[CoCl_4]$  (**1**) and  $[CoLCl_3]$  (**2**).

	$[CoCl_4]^{2-}$	$[CoLCl_3]$
Energies of terms / $cm^{-1}$	$0({}^4A_2)^a$	$0({}^4A_2)^a$
	3188( ${}^4T_2$ ) 3344 3617	3511( ${}^4T_2$ ) 3853 4538
	5682( ${}^4T_1$ ) 6019 6182	4882( ${}^4T_1$ ) 8273 8600
	18400( ${}^4T_1$ ) 18442 18654	18085( ${}^4T_1$ ) 19125 20909
Energies of spin-orbit multiplets of the ground term / $cm^{-1}$	0 8.1	0 41.5
$g_{1,2,3}$	2.314, 2.355, 2.367	2.161, 2.324, 2.404
$D/hc$ / $cm^{-1}$	3.96	19.9
$E/D$	0.12	0.17

<sup>a</sup> Assignment of the terms in  $T_d$  symmetry.



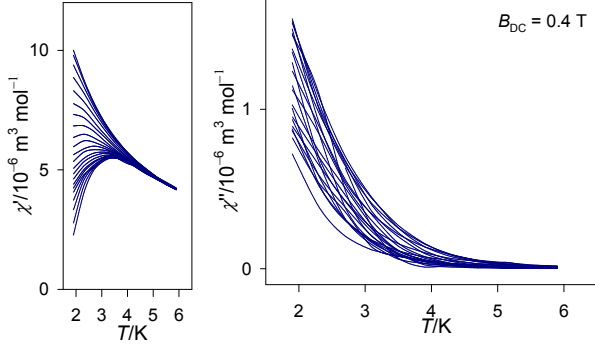
**Figure S4.** CASSCF/NEVPT2 magnetic functions for  $[L]_2[CoCl_4]$  (**1**).

**Table S3.** Individual contributions to *D*-tensor in [L]<sub>2</sub>[CoCl<sub>4</sub>] (**1**) and [CoLCl<sub>3</sub>] (**2**).

[CoCl <sub>4</sub> ] <sup>2-</sup>					[CoLCl <sub>3</sub> ]				
Block	Mult	Root	D	E	Block	Mult	Root	D	E
0	4	0	-0.000	0.000	0	4	0	0.000	0.000
0	4	1	<b>15.236</b>	15.972	0	4	1	<b>5.697</b>	9.798
0	4	2	<b>14.281</b>	-14.559	0	4	2	<b>3.186</b>	6.106
0	4	3	<b>-25.361</b>	-0.891	0	4	3	<b>9.863</b>	-12.504
0	4	4	0.001	-0.002	0	4	4	0.113	0.057
0	4	5	0.007	0.006	0	4	5	0.152	0.154
0	4	6	-0.003	-0.001	0	4	6	0.075	-0.101
0	4	7	-0.000	-0.000	0	4	7	0.004	-0.007
0	4	8	0.000	0.000	0	4	8	0.011	0.011
0	4	9	0.000	-0.000	0	4	9	0.001	0.001
1	2	0	0.000	0.002	1	2	0	0.132	0.179
1	2	1	-0.002	0.000	1	2	1	-0.021	0.008
1	2	2	-0.027	0.016	1	2	2	0.005	0.006
1	2	3	0.004	0.002	1	2	3	-0.073	-0.101
1	2	4	-0.012	-0.003	1	2	4	-0.022	-0.021
1	2	5	0.000	0.000	1	2	5	0.064	0.004
1	2	6	-1.790	-2.377	1	2	6	6.245	-0.423
1	2	7	-1.875	2.024	1	2	7	-0.213	-1.657
1	2	8	3.799	0.263	1	2	8	-1.847	1.893
1	2	9	-0.023	-0.009	1	2	9	-0.087	-0.084
1	2	10	0.009	0.011	1	2	10	0.057	0.007
1	2	11	0.002	-0.012	1	2	11	-0.173	-0.173
1	2	12	-0.240	-0.227	1	2	12	-0.006	0.030
1	2	13	-0.204	0.210	1	2	13	0.005	0.003
1	2	14	0.388	0.014	1	2	14	-0.015	-0.005
1	2	15	-0.003	0.003	1	2	15	-0.393	0.391
1	2	16	-0.005	-0.004	1	2	16	-0.003	-0.001
1	2	17	-0.000	-0.000	1	2	17	-0.158	-0.155
1	2	18	0.001	-0.000	1	2	18	-0.000	-0.002
1	2	19	-0.001	0.001	1	2	19	0.023	0.002
1	2	20	0.002	0.000	1	2	20	0.006	-0.000
1	2	21	0.003	0.000	1	2	21	-0.004	-0.005
1	2	22	-0.000	-0.000	1	2	22	1.555	0.010
1	2	23	1.321	-0.060	1	2	23	-0.034	-0.031
1	2	24	-0.703	-0.345	1	2	24	-0.620	0.654
1	2	25	-0.468	0.437	1	2	25	-0.498	-0.468
1	2	26	-0.000	-0.000	1	2	26	-0.011	0.012
1	2	27	-0.000	0.000	1	2	27	-0.052	-0.050
1	2	28	-0.000	-0.000	1	2	28	-0.003	-0.003
1	2	29	-0.002	-0.045	1	2	29	0.099	0.019
1	2	30	-0.034	-0.049	1	2	30	-0.123	-0.124
1	2	31	0.013	0.092	1	2	31	-0.120	0.129
1	2	32	-0.001	-0.000	1	2	32	-0.001	-0.006
1	2	33	0.000	0.001	1	2	33	-0.008	-0.006
1	2	34	-0.000	-0.000	1	2	34	-0.030	-0.029
1	2	35	-0.000	-0.000	1	2	35	-0.000	-0.000
1	2	36	-0.000	-0.000	1	2	36	0.006	0.007
1	2	37	0.008	0.015	1	2	37	-0.011	-0.010
1	2	38	0.003	-0.000	1	2	38	0.007	0.002
1	2	39	-0.004	-0.014	1	2	39	0.082	0.003

### AC magnetic data

The temperature evolution of the AC susceptibility components of **1** at fixed  $B_{DC} = 0.4$  T is shown in Fig. S5 for a set of frequencies  $f = 0.1 - 1500$  Hz. The individual frequency components  $\chi'$  merge at  $T \sim 5$  K, which can be assigned as a blocking temperature;  $\chi''$  vanishes concurrently.



**Figure S5.** Temperature dependence of the AC susceptibility components of **1** for frequencies  $f = 0.1 - 1500$  Hz at  $B_{DC} = 0.4$  T.

The AC susceptibility data (22 points for  $\chi'$  and 22 points for  $\chi''$ ) have been fitted to the extended three-set and two-set Debye models for **1** and **2**, respectively

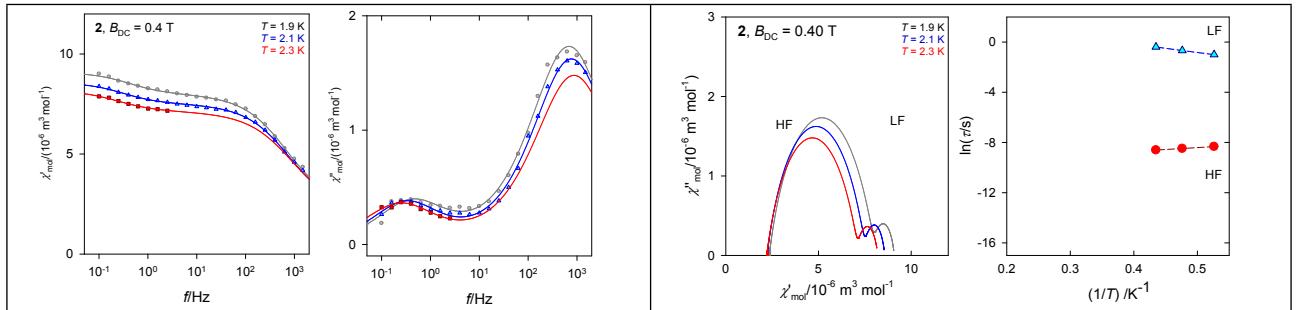
$$\chi(\omega) = \chi_S + \sum_{k=1}^3 \frac{\chi_{Tk} - \chi_S}{1 + (i\omega\tau_k)^{1-\alpha_k}}$$

containing up to 10 free parameters: the isothermal susceptibilities  $\chi_{Tk}$ , the distribution parameters  $\alpha_k$  and the relaxation times  $\tau_k$  for each relaxation channel, along with the adiabatic susceptibility  $\chi_S$ . The above equation can be decomposed into the real and imaginary components, e.g.

$$\chi'(\omega) = \chi_S + (\chi_{T1} - \chi_S) \frac{1 + (\omega\tau_1)^{1-\alpha_1} \sin(\pi\alpha_1/2)}{1 + 2(\omega\tau_1)^{1-\alpha_1} \sin(\pi\alpha_1/2) + (\omega\tau_1)^{2-2\alpha_1}} + (\chi_{T2} - \chi_{T1}) \frac{1 + (\omega\tau_2)^{1-\alpha_2} \sin(\pi\alpha_2/2)}{1 + 2(\omega\tau_2)^{1-\alpha_2} \sin(\pi\alpha_2/2) + (\omega\tau_2)^{2-2\alpha_2}} + \dots$$

$$\chi''(\omega) = (\chi_{T1} - \chi_S) \frac{(\omega\tau_1)^{1-\alpha_1} \cos(\pi\alpha_1/2)}{1 + 2(\omega\tau_1)^{1-\alpha_1} \sin(\pi\alpha_1/2) + (\omega\tau_1)^{2-2\alpha_1}} + (\chi_{T2} - \chi_{T1}) \frac{(\omega\tau_2)^{1-\alpha_2} \cos(\pi\alpha_2/2)}{1 + 2(\omega\tau_2)^{1-\alpha_2} \sin(\pi\alpha_2/2) + (\omega\tau_2)^{2-2\alpha_2}} + \dots$$

which are fitted simultaneously by minimizing a joint functional  $F = w \cdot E(\chi') + (1-w) \cdot E(\chi'')$ .



**Figure S6.** Frequency dependences of the AC susceptibility components of **2** for a set of temperatures at  $B_{DC} = 0.4$  T. Solid lines – fitted with a two-set Debye model.

**Table S4.** Field dependences of the AC susceptibility parameters for **1** at  $T = 2.0$  K.<sup>a</sup>

$B_{DC}/T$	$R(\chi')$ /%	$R(\chi'')$ /%	$\chi_{LF}$	$\alpha_{LF}$	$\tau_{LF}$ /s	$\chi_{IF}$	$\alpha_{IF}$	$\tau_{IF}$ / $10^{-3}$ s	$\chi_{HF}$	$\alpha_{HF}$	$\tau_{HF}$ / $10^{-6}$ s	$x_{LF}$	$x_{IF}$	$x_{HF}$
0.2	0.74	3.0	0.99	.07	<b>0.15(5)</b>	2.1(1)	.08	15(5)	10.3(1)	.22	142(4)	.10	.11	.80
0.4	0.91	4.2	1.50	.01	<b>0.30(5)</b>	5.1(3)	.33	34(20)	9.6(1)	.25	77(4)	.16	.37	.47
0.6	1.5	6.7	2.9	.10	<b>0.38(5)</b>	6.2(7)	.44	46	8.8(4)	.15	23(4)	.33	.37	.30
0.8	1.2	6.8	2.6	.00	<b>0.50(3)</b>	5.3(8)	.42	83	7.5(5)	.54	2.3	.35	.36	.29
1.0	2.2	7.3	2.8	.02	<b>0.54(4)</b>	4.8(10)	.53	63	6.3(8)	.17	0.85	.44	.31	.24
1.2	6.0	13	2.5	.01	<b>0.54(11)</b>	3.3(5)	.21	45	4.9(2)	.59	1.9	.52	.15	.33

<sup>a</sup> Obtained by a three-set Debye model;  $\chi$  in units of  $10^{-6}$  m<sup>3</sup> mol<sup>-1</sup>;  $\chi_S = 0$ .

$$x_{LF} = (\chi_{T,LF} - \chi_S) / (\chi_T - \chi_S), \quad x_{IF} = (\chi_{T,IF} - \chi_{T,LF}) / (\chi_T - \chi_S), \quad x_{HF} = (\chi_{T,HF} - \chi_{T,IF}) / (\chi_T - \chi_S), \quad \chi_{T,HF} = \chi_T.$$

**Table S5.** Field dependences of the AC susceptibility parameters for **2** at  $T = 1.9$  K.<sup>a</sup>

$B_{DC}/T$	$R(\chi')$ /%	$R(\chi'')$ /%	$\chi_S$	$\chi_{LF}$	$\alpha_{LF}$	$\tau_{LF}$ /s	$\chi_{IF}$	$\alpha_{IF}$	$\tau_{IF}$ / $10^{-3}$ s	$\chi_{HF}$	$\alpha_{HF}$	$\tau_{HF}$ / $10^{-6}$ s	$x_{LF}$	$x_{IF}$	$x_{HF}$
0.2	0.27	1.3	2.4	2.6(3)	.02	<b>0.45(7)</b>	4.7(5)	.04	1.1(1)	9.8(1)	.38	94(22)	.03	.28	.69
0.4	0.49	3.1	0.6	1.6(20)	.26	<b>0.38(5)</b>	3.1(12)	.01	0.5(1)	9.1(1)	.46	53	.13	.17	.71
0.6	0.64	4.0	0	1.5(3)	.14	<b>0.81(10)</b>	2.0(1)	.02	51(16)	8.2(1)	.42	48(2)	.19	.05	.76
0.8	0.70	2.0	0	1.5(6)	.01	<b>1.24(8)</b>	3.2(2)	.43	97	7.8(1)	.37	21(10)	.20	.21	.59
1.0	1.3	2.0	0	1.5	.01	<b>1.43(23)</b>	3.4(9)	.54	147	6.8(6)	.37	8.4(21)	.22	.28	.50
1.2	0.74	3.0	0	1.8(10)	.11	<b>1.82(20)</b>	2.9(3)	.49	123	5.7(2)	.60	1.9(7)	.32	.19	.49
1.4	1.9	5.7	0	1.2	.03	<b>1.52(64)</b>	2.5(26)	.60	216	4.6	.50	1.6	.26	.28	.46

<sup>a</sup> Obtained by a three-set Debye model;  $\chi$  in units of  $10^{-6}$  m<sup>3</sup> mol<sup>-1</sup>.

**Table S6.** Results of the fitting procedure for the AC susceptibility components of **1** at  $B_{DC} = 0.4$  T.<sup>a</sup>

$T/K$	$R(\chi')$ /%	$R(\chi'')$ /%	$\chi_{LF}$	$\alpha_{LF}$	$\tau_{LF}$ /s	$\chi_{IF}$	$\alpha_{IF}$	$\tau_{IF}$ / $10^{-3}$ s	$\chi_{HF}$	$\alpha_{HF}$	$\tau_{HF}$ / $10^{-6}$ s	$x_{LF}$	$x_{IF}$	$x_{HF}$
1.9	0.77	2.8	1.5(13)	.01	<b>0.39(4)</b>	6.1(4)	.40	49(32)	10.4(2)	.25	90(4)	.15	.44	.41
2.0	0.91	4.2	1.50	.01	0.30(5)	5.1(3)	.33	34(20)	9.6(1)	.25	77(4)	.16	.37	.47
2.3	0.71	2.8	1.0(6)	.05	0.18(2)	4.6(2)	.50	30(17)	9.1(1)	.07	33(1)	.11	.40	.49
2.7	0.58	3.2	1.2(5)	.10	0.17(2)	2.8(1)	.40	10(7)	7.8(1)	.04	11(2)	.15	.20	.64
3.1	0.27	2.7	0.86(19)	.10	0.16(1)	1.6(1)	.40	7.7(36)	7.0(1)	.01	4.3(13)	.12	.11	.77
3.5	0.26	5.2	0.35(5)	.10	0.19(2)	0.51(6)	.37	2.5(15)	5.8(1)	.01	0.10	.06	.03	.91

<sup>a</sup> Obtained by a three-set Debye model;  $\chi$  in units of  $10^{-6}$  m<sup>3</sup> mol<sup>-1</sup>; fixed  $\chi_S = 5.0 \times 10^{-6}$  m<sup>3</sup> mol<sup>-1</sup>.

**Table S7.** Results of the fitting procedure for the AC susceptibility components of **2** at  $B_{DC} = 0.4$  T.<sup>a</sup>

$T/K$	$R(\chi')$ /%	$R(\chi'')$ /%	$\chi_S$	$\chi_{LF}$	$\alpha_{LF}$	$\tau_{LF}$ /s	$\chi_{HF}$	$\alpha_{HF}$	$\tau_{HF}$ / $10^{-6}$ s	$x_{LF}$
1.9	0.73	4.2	2.3(2)	3.4(2)	.24	<b>0.38(5)</b>	9.1(1)	.30	231(13)	.16
2.1	0.57	3.2	2.3(1)	3.3(2)	.24	0.51(6)	8.6(1)	.30	206(9)	.17
2.3	0.29	3.6	2.2	3.3	.27	0.67	8.2	.31	183	.18

<sup>a</sup> Obtained by a two-set Debye model;  $\chi$  in units of  $10^{-6}$  m<sup>3</sup> mol<sup>-1</sup>.

**Table S8.** Crystallographic data for [L]<sub>2</sub>[CoCl<sub>4</sub>] (**1**) and [CoLCl<sub>3</sub>] (**2**).

Compound	<b>1</b>	<b>2</b>
Empirical formula	C <sub>26</sub> H <sub>24</sub> Cl <sub>4</sub> CoN <sub>6</sub>	C <sub>13</sub> H <sub>12</sub> Cl <sub>3</sub> CoN <sub>3</sub>
Formula weight	621.24	375.54
T/K	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2</i> <sub>1</sub> / <i>n</i>	<i>C2/c</i>
<i>a</i> /Å	7.56350(10)	30.956(2)
<i>b</i> /Å	22.0902(4)	7.5909(2)
<i>c</i> /Å	16.0872(4)	14.5621(6)
β/°	100.009(2)	116.232(4)
<i>V</i> /Å <sup>3</sup>	2646.93(9)	3069.4(3)
<i>Z</i>	4	8
D <sub>cal</sub> /g cm <sup>-3</sup>	1.559	1.625
μ/mm <sup>-1</sup>	1.081	1.632
Reflections collected	28159	10596
Independent reflections	8611 [ <i>R</i> (int) = 0.0489]	3422 [ <i>R</i> (int) = 0.0317]
Data / restraints / parameters	8611 / 0 / 336	3422 / 0 / 182
GOF	1.027	1.063
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0397	0.0331
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0828	0.0713
<i>R</i> <sub>1</sub> (all data)	0.0580	0.0431
<i>wR</i> <sub>2</sub> (all data)	0.0887	0.0763
Δρ <sub>max/min</sub> /e.Å <sup>-3</sup>	0.582 and -0.437	0.462 and -0.318
CCDC number	1903683	1903684

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