Electronic Supplementary Material (ESI) for Dalton Transactions.

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"Slow magnetic relaxation for cobalt(II) complexes in axial bipyramidal environment: an S = ½ spin case."

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1- Characterization.

2-Structural aspects.

3-Magnetic data.

1- Characterization.

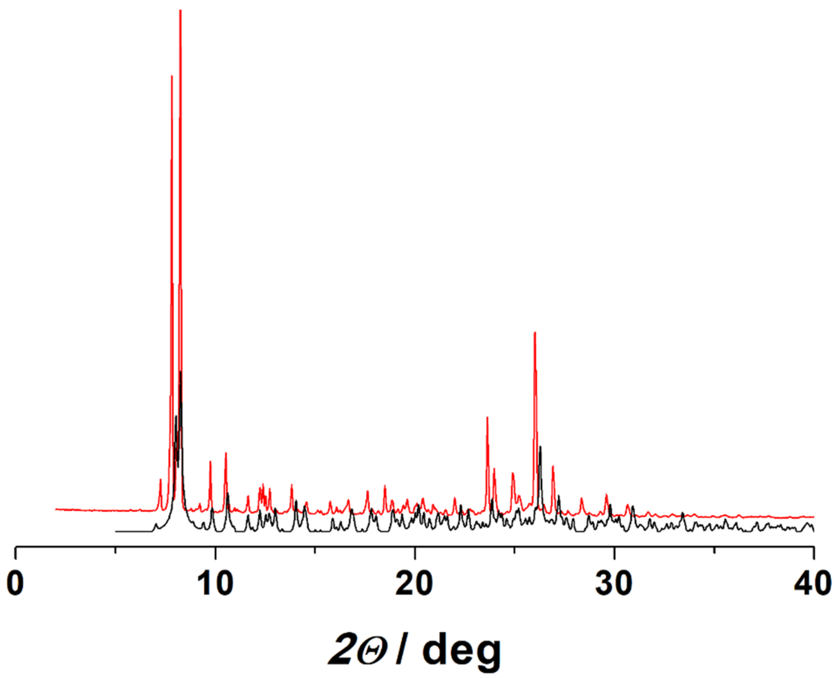

Fig. S1. Powder X-ray spectra of the reference complex **1** (black line) and its diluted analogous **1D**.

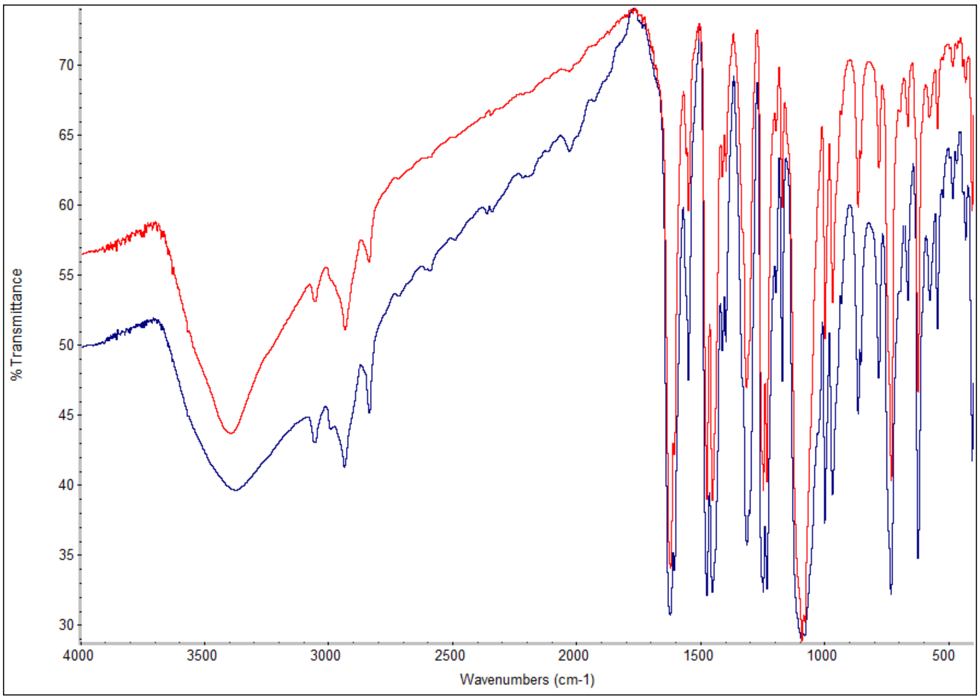

Fig. S2. IR spectra for complexes **1** (red) and **1D**. Characteristic bands: st. C-H 3000-2800 cm^{-1}; N=C iminic ~1600 cm^{-1}; st. ClO_4^- 1075 cm^{-1}; δ ClO_4^- 620 cm^{-1}.

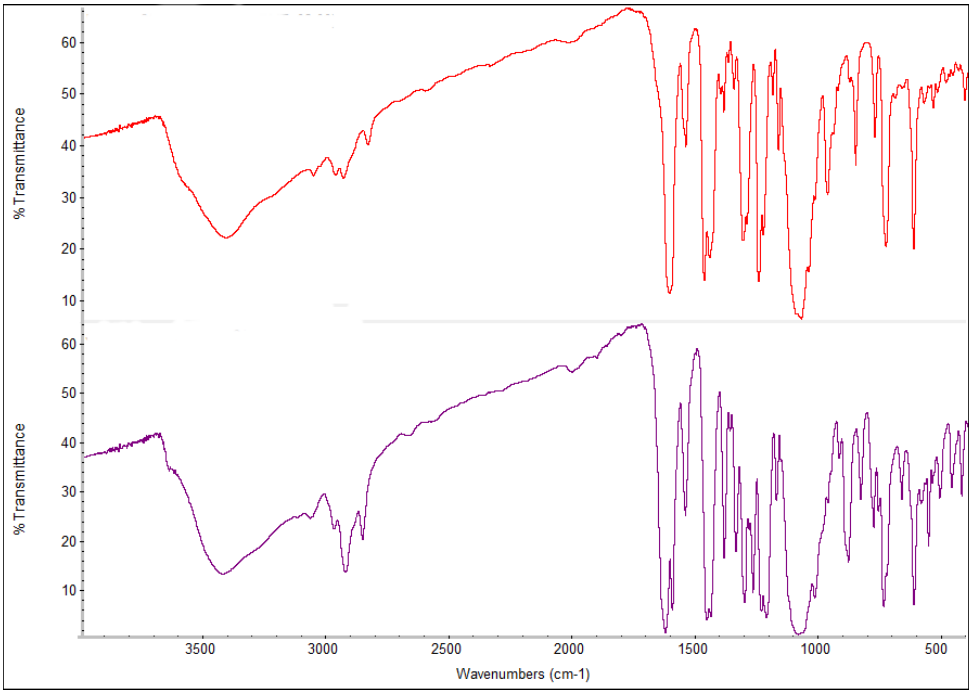

Fig. S3. IR spectra for complexes **2** (top) and **3** (bottom).

2-Structural aspects.

Table S1. SHAPE measures for the Co^{II} cation of complex **1**. *S*(*P*) = 0 corresponds to a structure fully coincident in shape with the reference polyhedron P, regardless of size and orientation. The closest polyhedron is highlighted in red.

S(vOC-5)	6.80	*S*(PBPY-7)	**1.64**
S(TBPY-5)	6.82	*S*(COC-7)	8.17
S(SPY-5)	6.79	*S*(CTPR-7)	6.59
S(JTBPY-5)	8.81	*S*(JPBPY-7)	3.60

Ideal ML_5 polyhedra: vOC-5 (C_4v) Vacant octahedron; TBPY-5 (D_3h) Trigonal bipyramid; SPY-5 (C_4v) Spherical square pyramid; JTBPY-5 (D_3h) Johnson trigonal bipyramid J12.
Ideal ML_7 polyhedra: PBPY-7 (D5h) Pentagonal bipyramid; COC-7 (C3v) Capped octahedron; CTPR-7 (C2v) Capped trigonal prism; JPBPY-7 (D5h) Johnson pentagonal bipyramid J13; JETPY-7 (C3v) Johnson elongated triangular pyramid J7.

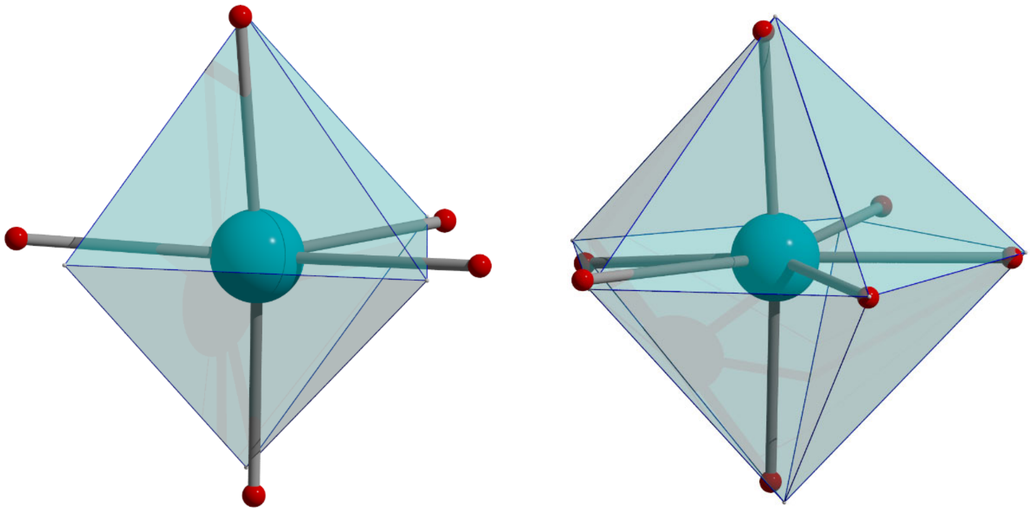

Fig. S4. Plot of the coordination sphere of the Co^{II} cation for complex **1**, referenced to the ideal polyhedra trigonal bipyramid (left) and pentagonal bipyramid (right).

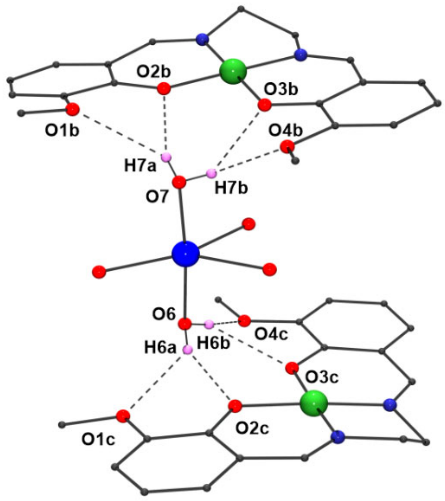

Fig. S5. Detail of the H-bonds promoted by the axially coordinated water molecules and the capping [NiL1] fragments for complex **1**.

Table S2. Bond parameters for the bifurcated H-bonds corresponding to complex **1**.

	d O···O' (Å)		*d* H···O' (Å)		O-H···O (deg.)
O6···O1c	2.976(4)	H6a-O1c	2.29(3)	O6-H6a···O3c	127(2)
O6···O2c	2.761(4)	H6a-O2c	2.10(2)	O6-H6a···O4c	159(3)
O6···O3c	2.848(4)	H6b-O3c	2.35(3)	O6-H6b···O1c	135(3)
O6···O4c	2.861(4)	H6b-O4c	2.03(2)	O6-H6b···O2c	152(3)
O7···O1b	3.010(4)	H7a-O1b	2.46(3)	O7-H7a···O1b	127(3)
O7···O2b	2.804(4)	H7a-O2b	2.04(3)	O7-H7a···O2b	160(3)
O7···O3b	2.860(4)	H7b-O3b	2.34(4)	O7-H7b···O3b	123(3)
O7···O4b	2.971(5)	H7b-O4b	2.20(4)	O7-H7b···O4b	161(3)

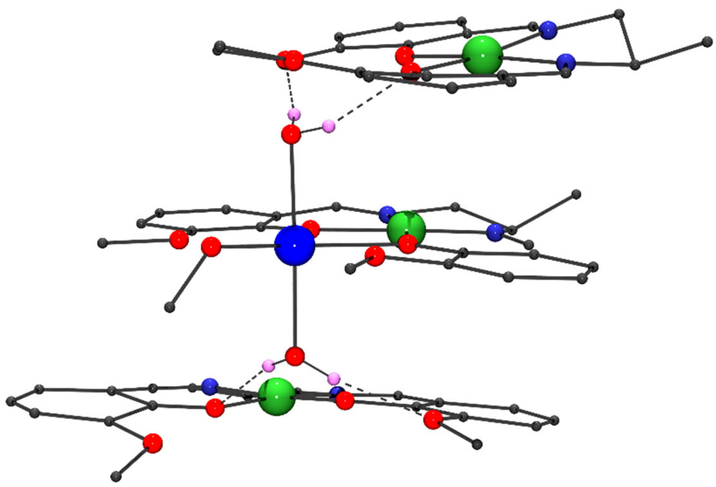

Fig. S6. Molecular structure of complex **2*R*** from the partial structure resolution.

3-Magnetic data.

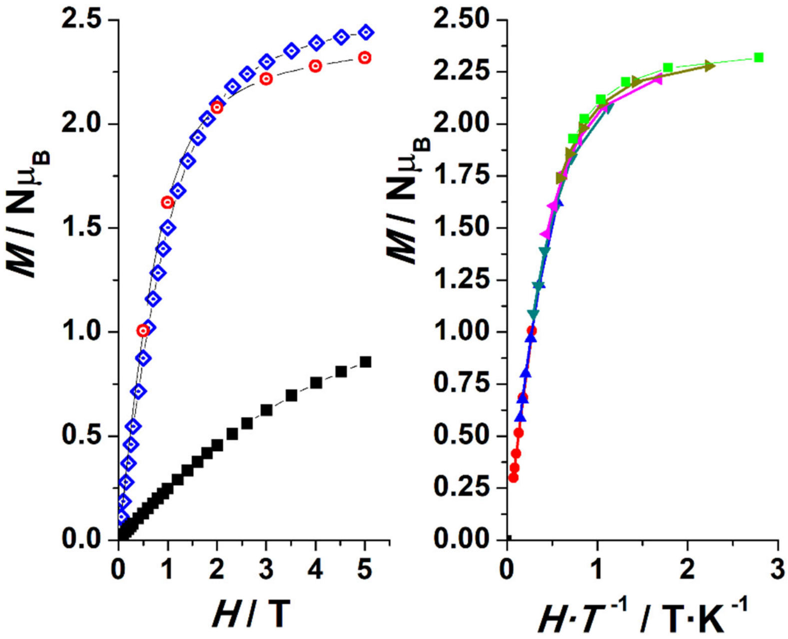

Fig. S7. Left, magnetization *vs*. field for complexes **1** (red circles), **2*R*** (blue diamonds) and **3*SS*** (black squares). Right, reduced magnetization for complex **1** showing the superimposable plots in the 1.8-6.8 range of temperature (increment 1 K).

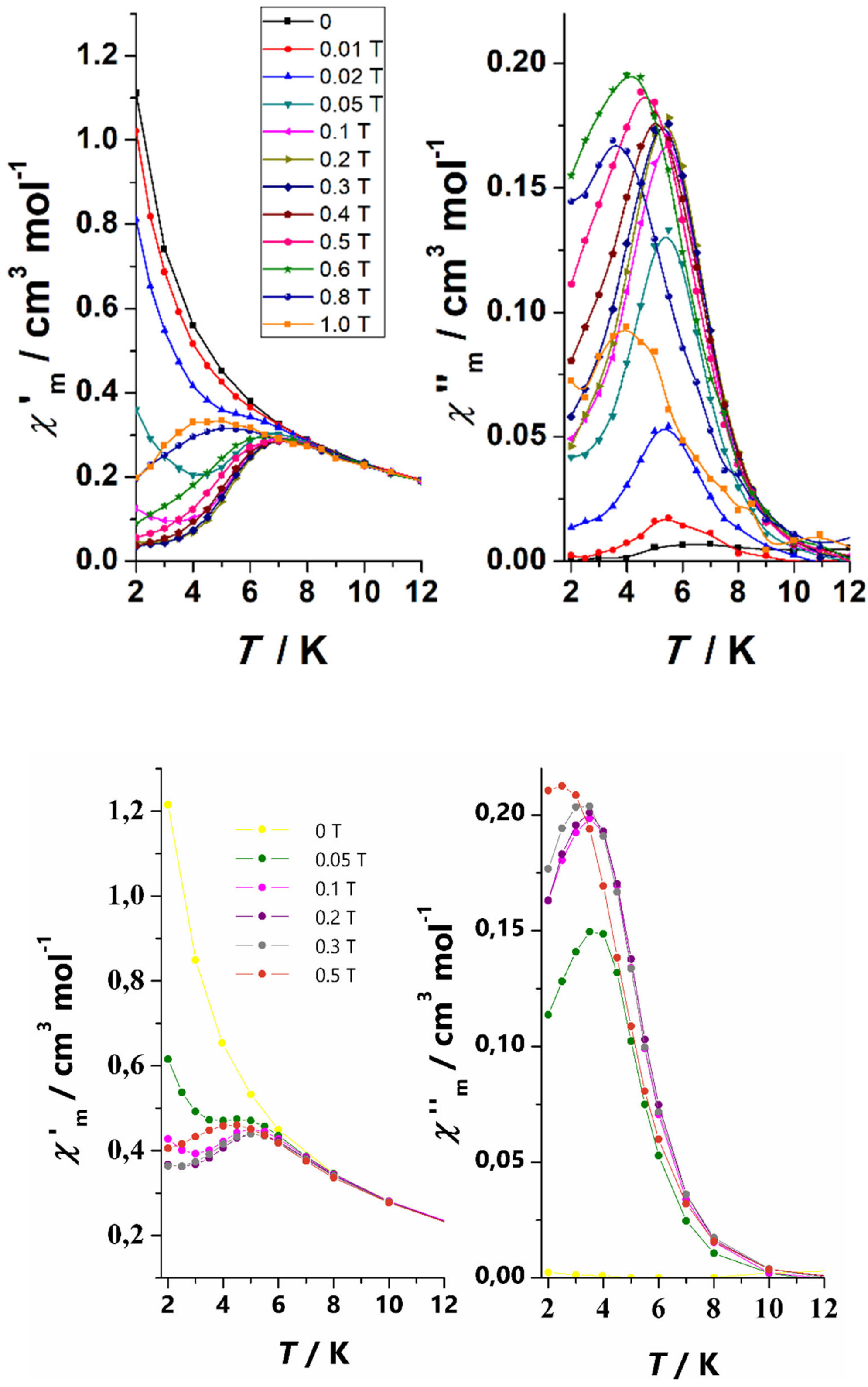

Fig. S8. χ_M'' dependence of the transverse field for complexes **1** (top) and **2*R*** (bottom).

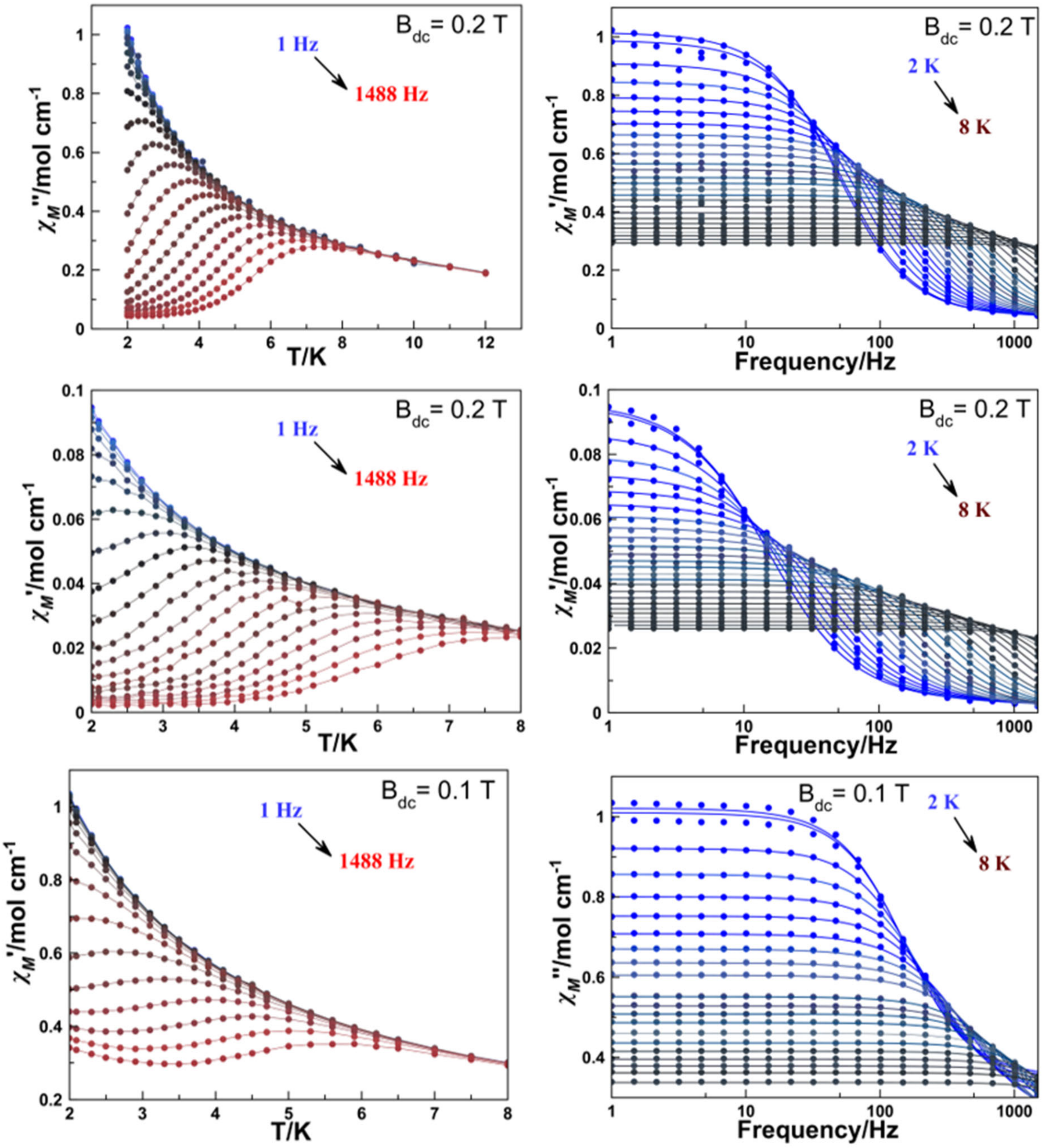

Fig. S9. χ_M'(T) and . χ_M'(υ) for complexes **1**, **1D** and **2*R***.

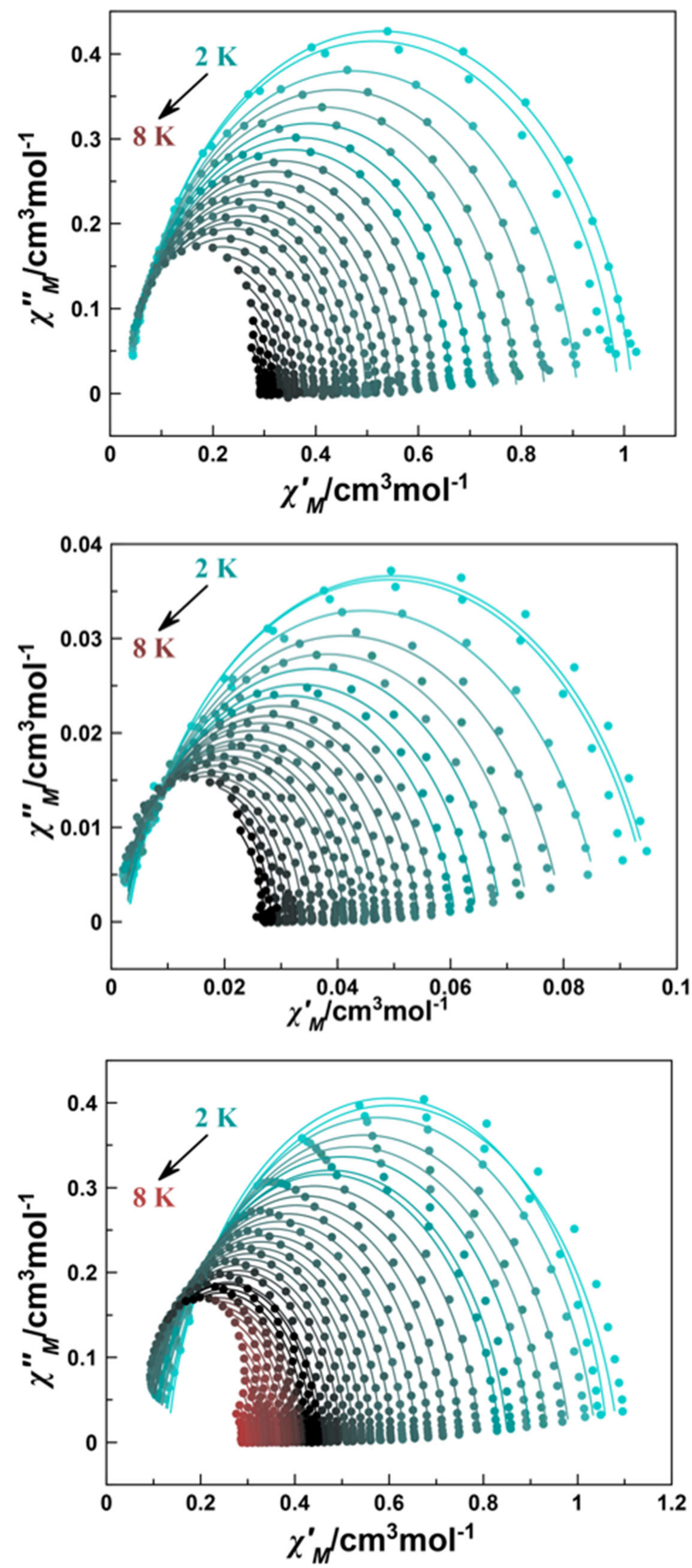

Fig. S10. Argand plots for complexes **1**, **1D** and **2*R*.** Solid lines show the best fit of the experimental data.

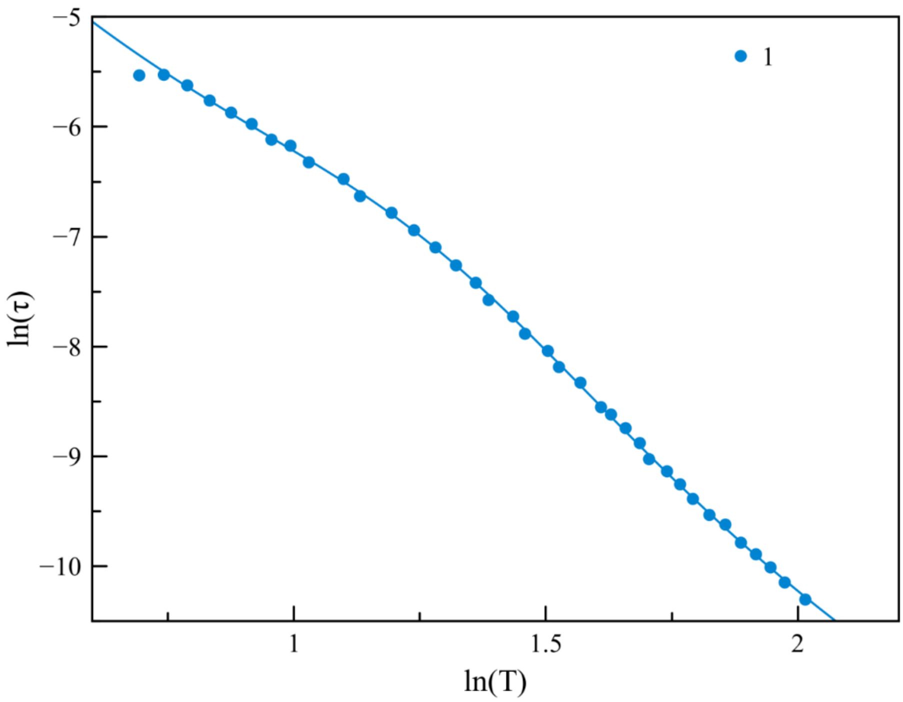

Fig. S11. Temperature dependence of the relaxation time of **1** plotted in log-log scale. The two different slopes at low and high temperature hints at dominant direct and Raman processes in the two temperature regions.

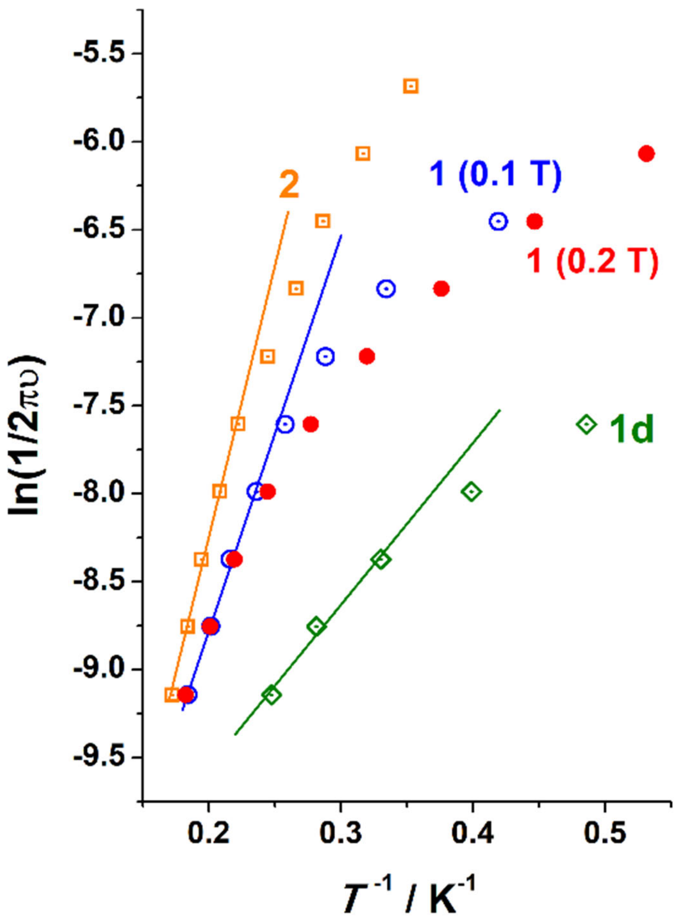

Fig. S12. Plot of ln(1/2πν) vs. T^{-1} from the χ_M''(T) data for complexes **1**, **1D** and **2*R***. The data are limited to the HF region for which the maxima of χ_M'' can be observed.

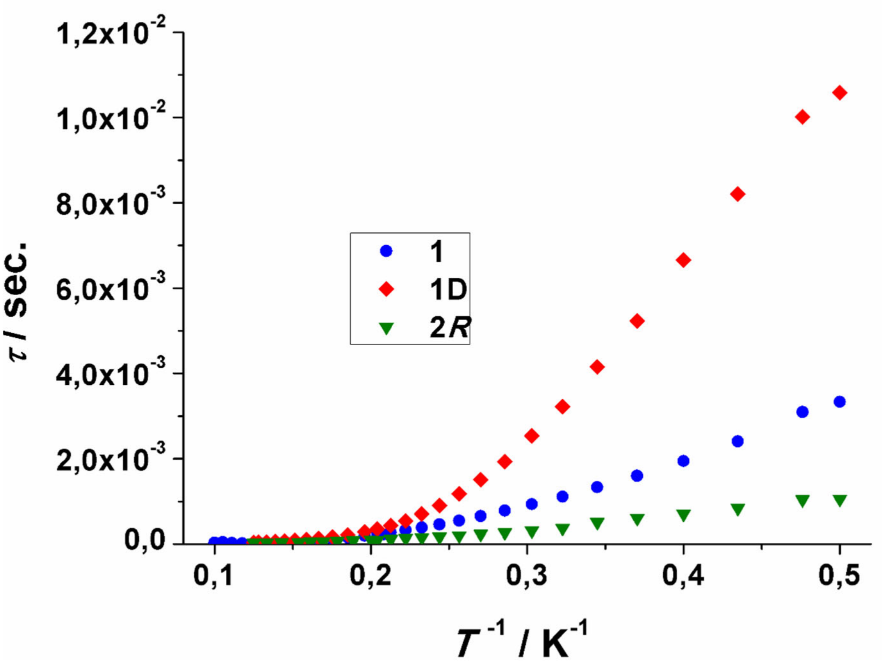

Fig. S13. Plot of τ *vs*. inverse of temperature showing the lowtemperature increase of *t* for the diluted complex **1D**.