Electronic Supplementary Information for Dalton Transactions

Magnetic anisotropy of two trinuclear and tetranuclear $Ni^{II}Cr^{III}$ cyanide-bridged complexes with spin ground states S = 4 and 5

Jean-Noël Rebilly,[a] Laure Catala,[a] Gaëlle Charron,[a] Guillaume Rogez,[a,c] Eric Rivière,[a] Régis Guillot,[a] Anne-Laure Barra [b] and Talal Mallah *[a]

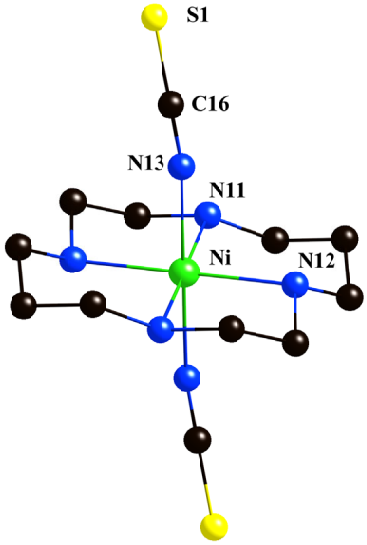

Fig. S1 view of the molecular structure of Ni(cyclam)$(NCS)_2$. The compound contains four cristallographically independent molecules with very slight structural differences, only one complex is depicted here

Table S1 Selected bond lengths [Å] and angles [°] for one Ni(cyclam)$(NCS)_2$.
The other molecules have very small angles and dond lengths diferrence

NiN11 2.069	NiN12 2.064	NiN13 2.16
N11NiN12 95.04	N11NiN12' 84.96	

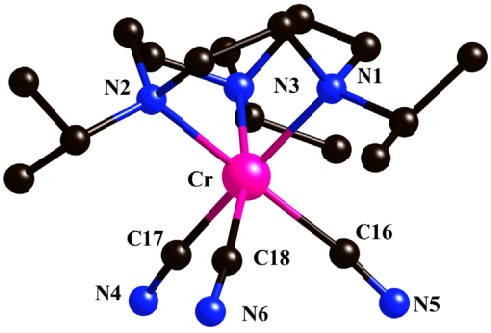

Fig. S2 view of the molecular structure of the Cr(iPrtacn)$(CN)_3$ complex

Table S2 Selected bond lengths [Å] and angles [°] for Cr(iPrtacn))$(CN)_3$

CrN1	2.160	CrN2	2.185	CrN3	2.173
CrC16	2.072	CrC17	2.063	CrC18	2.064
N1CrN2	84.19	N1CrN3	84.11	N2CrN3	84.33
C16CrC17	84.62	C16CrC18	83.94	C17CrC18	86.19

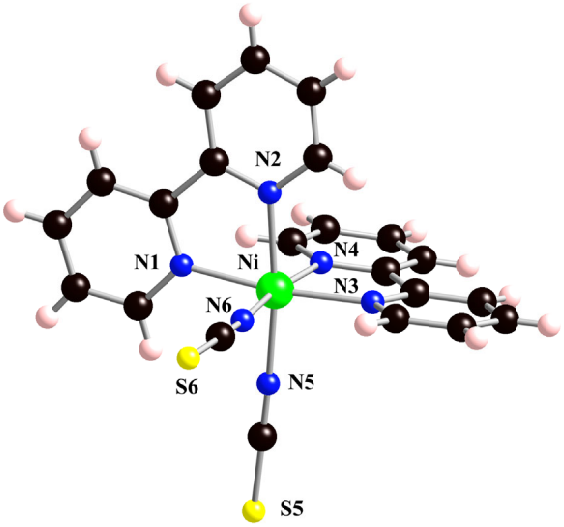

Fig. S3 view of the molecular structure of $Ni(bpy)_2(NCS)$

Table S3 Selected bond lengths [Å] and angles [°] for $Ni(bpy)(NCS)_2$			
NiN1 2.083	NiN2 2.107	NiN3 2.086	
NiN4 2.103	NiN5 2.064	NiN6 2.033	
N1NiN2 78.29	N1NiN3 171.57	N1NiN4 95.68	N1NiN5 93.53
N1NiN6 91.67	N2NiN3 95.58	N2NiN4 90.03	N2NiN5 171.38
N2NiN6 91.91	N3NiN4 78.42	N3NiN5 92.28	N3NiN6 94.32
N4NiN5 88.07	N4NiN6 172.64	N5NiN6 91.04	

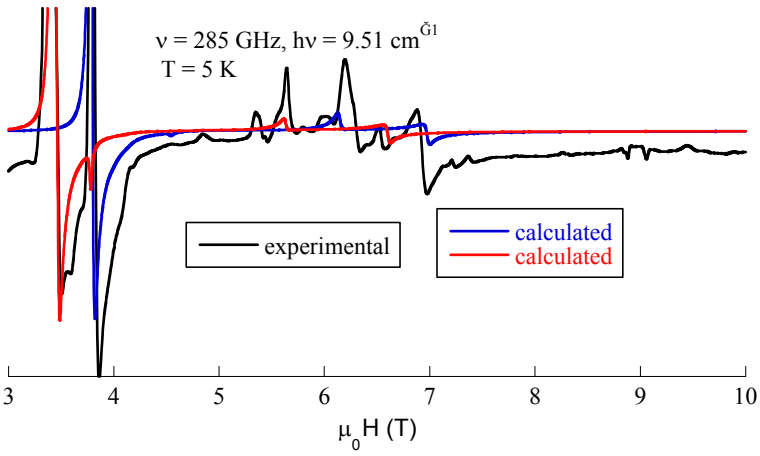

Fig S4 HF-HFEPR spectrum for $Ni(cyclam)(NCS)_2$ at 285 GHz. The experimental spectrum (black) has two resonances between 3 and 4 T (beta type resonances) that were assumed to correspond to two sets (with two molecules each) of enough structurally different Ni complex. Thus two different simulations were made in order to reproduce these two resonances. The calculated spectra are in red and blue.

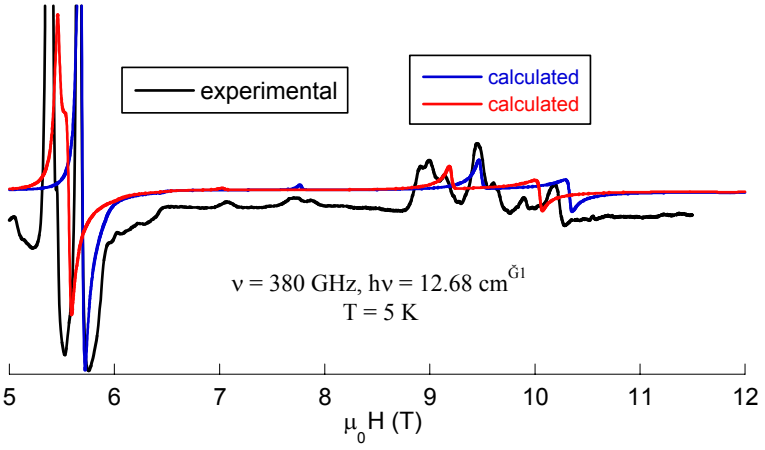

Fig S5 HF-HFEPR spectrum for Ni(cyclam)$(NCS)_2$ at 380 GHz (experimental, black). The red and blue spectra were calculated using the same parameters as for the 285 GHz frequency.

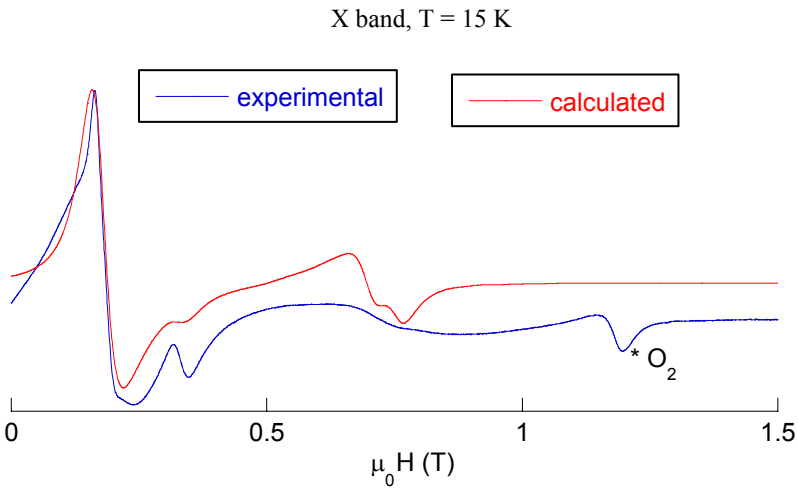

Fig S6 X-band spectrum of Cr(iPrtacn)$(CN)_3$ (blue) and calculated spectra (red).

Table S4 AOM parameters for Ni(cyclam)$(NCS)_2$ used to calculate the D and E values and to determine the **D** tensor orientation. The Racah parameters were taken equal to B = 860 cm^{-1} and C = 3350 cm^{-1}. the spin orbit parameter ζ = 630 cm^{-1}

Ni(cyclam)$(NCS)_2$	AOM parameters in cm^{-1}
N11	e_σ= 4726
N12	e_σ= 4726
N13	e_σ= 2520 e_π= –120
Calculated Hamiltonian parameters	D = 5.87 cm^{-1} E/D = 0.18
Experimental Hamiltonian parameters (from EPR)	D = 5. 8 cm^{-1} E/D = 0.07

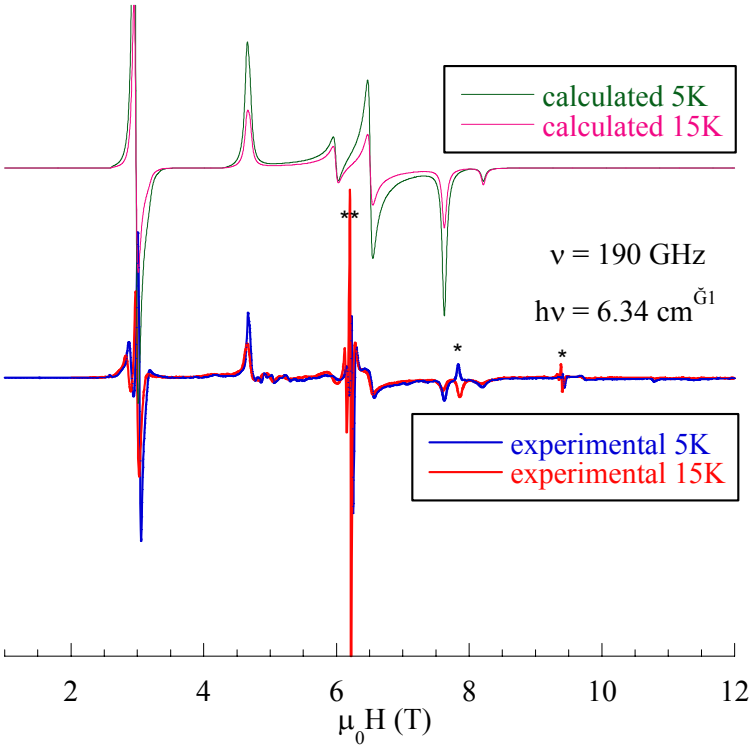

Fig. S7 Experimental and calculated HF–HFEPR spectra (T = 5 and 15 K) for $Ni(bpy)_2(NCS)_2$ at 190 GHz

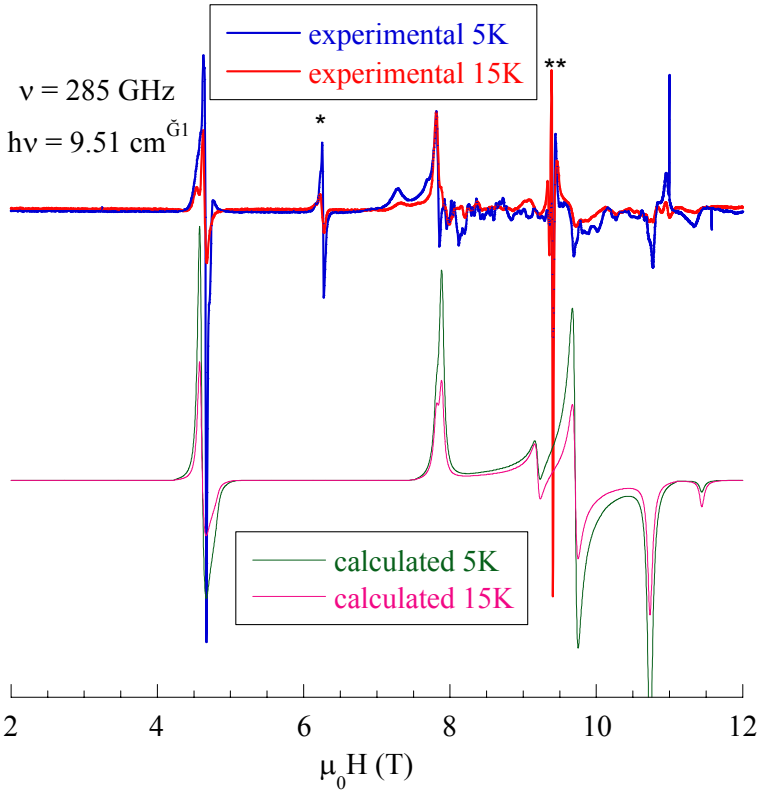

Fig. S8 Experimental and calculated HF–HFEPR spectra (T = 5 and 15 K) for $Ni(bpy)_2(NCS)_2$ at 285 GHz

Table S5 AOM parameters for $Ni(bpy)_2(NCS)_2$ used to calculate the D and E values and to determine the **D** tensor orientation. The Racah parameters were taken equal to B = 860 cm^{-1} and C = 3350 cm^{-1}. the spin orbit parameter ζ = 630 cm^{-1}

$Ni(bpy)_2(NCS)_2$	AOM parameters in cm^{-1}
N1	e_σ= 4511 e_π= 609
N3	e_σ= 4404 e_π= 592
N2	e_σ= 4199 e_π= 559
N4	e_σ= 4300 e_π= 575
N5	e_σ= 4543 e_π= 804
N6	e_σ= 4121 e_π= 715
Calculated Hamiltonian parameters	D = –1.61 cm^{-1} E/D = 0.26
Experimental Hamiltonian parameters (from EPR)	D = –1.74 cm^{-1} E/D = 0.24