Electronic Supplementary Information (ESI) A Chain of Vertex-sharing {CoIII2CoII2}n Squares with Single-Ion Magnet Behaviour

Maria-Gabriela Alexandru[1], Diana Visinescu[2], Sergiu Shova[3], Joan Cano[4], Nicolás Moliner[4], Francesc Lloret[4] and Miguel Julve[4]

[1] Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, Faculty of Chemical Engineering and Biotechnologies, University Politehnica of Bucharest, 1-7 Gh. Polizu Street, 011061 Bucharest, Romania, e-mail: alexandru.gabriela@gmail.com

[2] Coordination and Supramolecular Chemistry Laboratory, "Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, Splaiul Independentei 202, Bucharest 060021, Romania

[3] "Petru Poni" Institute of Macromolecular Chemistry, Romanian Academy, Aleea Grigore Ghica Vodă 41-A, RO-700487 Iasi, Romania

[4] Departament de Química Inorgànica/Instituto de Ciencia Molecular (ICMol), Universitat de València, 46980 Paterna, Valencia, Spain; e-mail: joan.cano@uv.es; francisco.lloret@uv.es
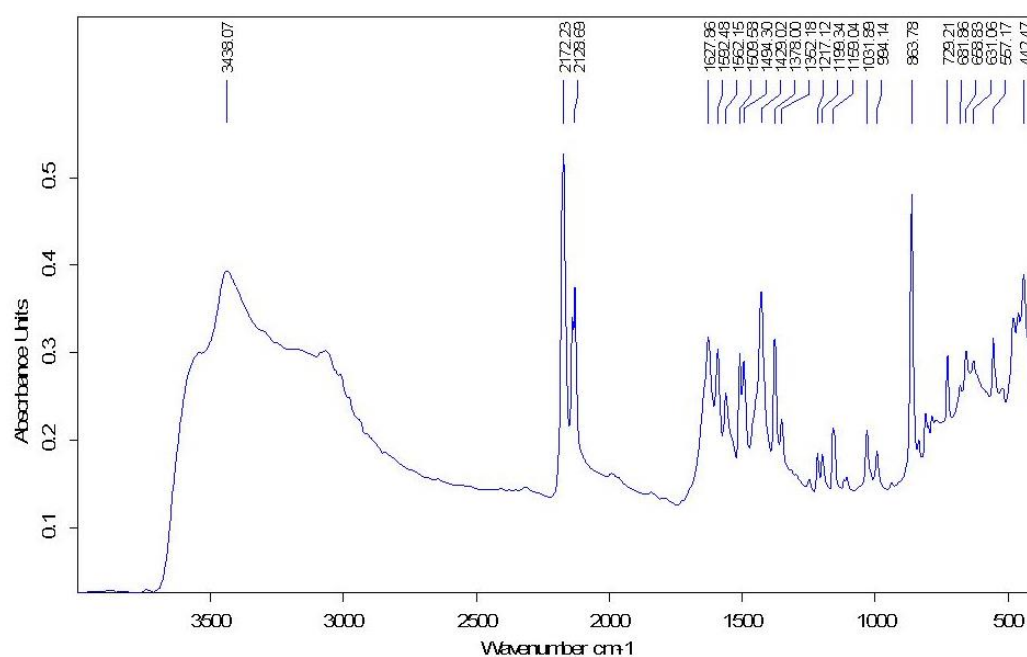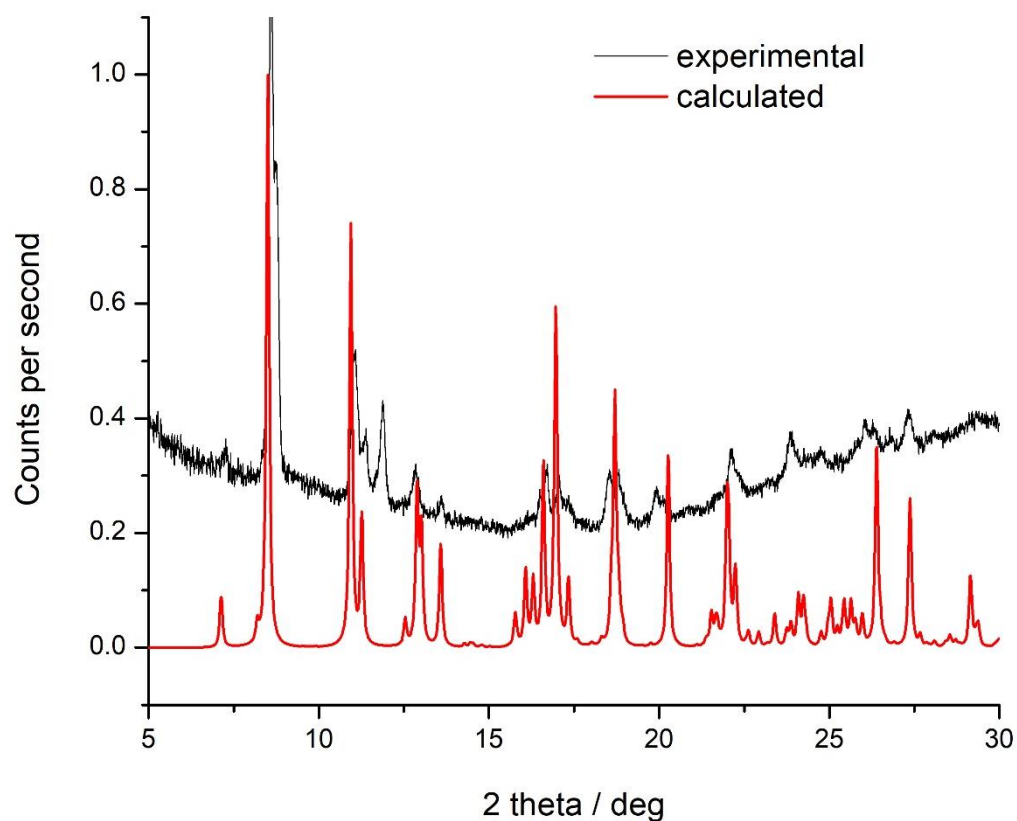
Figure S1. FTIR spectrum for **1.**

Figure S2. Experimental and calculated XRD patterns of **1**.

Table S1. Summary of the *SHAPE* analysis for the six-coordinated [$Co^{II}N_4O_2$] (Co1 atom) and [$Co^{III}C_4N_2$] (Co2 atom) fragments in **1**.

CN = 6[a]	Co1	Co2
HP-6	32.692	30.890
PPY-6	30.016	28.624
OC-6	**0.016**	**0.459**
TPR-6	16.464	15.781
JPPY-6	33.494	31.890

[a] PPY-6, C_{5v} Pentagonal pyramid; OC-6, O_h Octahedron; TPR-6, D_{3h} Trigonal prism; JPPY-5, C_{5v} Johnson pentagonal pyramid (J2).
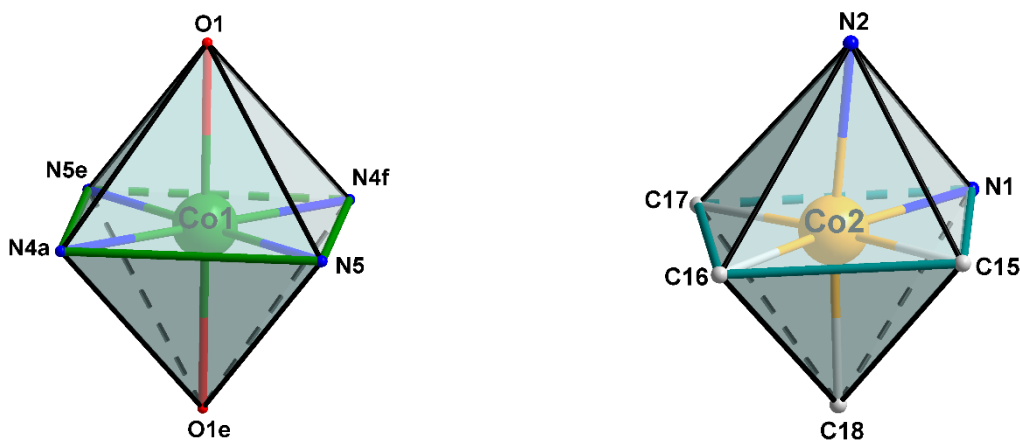
Figure S3. Coordination geometries of Co1 and Co2 atoms. [Symmetry codes: *a* = 1-*x*, 1-*y*, -*z*;   *e* = 2-*x*, 1-*y*, -*z*; *f* = 1+*x*, *y*, *z*].
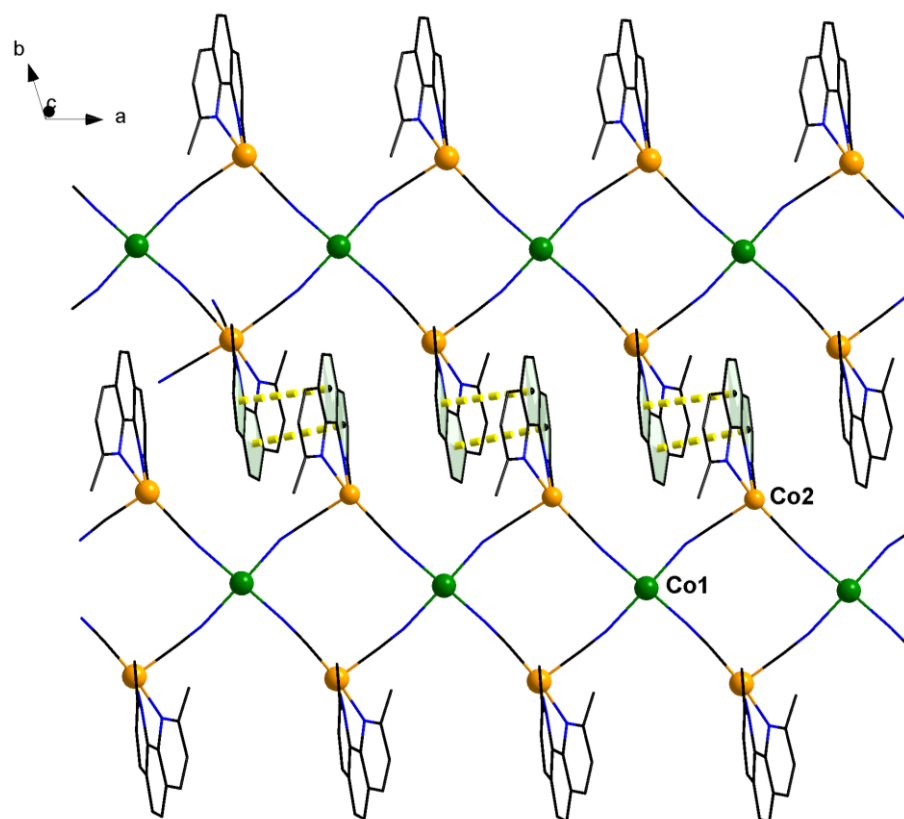
Figure S4. A view of the π-π stacking in **1.**

Table S2. Hydrogen-bonds for **1**[*]

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	Angle D-H···A
O1-H1···O1W	0.88	1.87	2.728(8)	163(3)
O1W-H1WA···N6[a]	0.86	1.99	2.848(10)	173.4
O1W-H1WB···N6[d]	0.85	2.08	2.935(10)	175.1

[*]Symmetry code: (a) = 1-x, 1-y, -z; (d) = x, 1+y, z.

Table S3. Atomic cartesian coordinates (Å) for molecular models A and B based on the experimental geometry of **1**.

|		Model A				Model B		
Atom	***x***	***y***	***z***	**Atom**	***x***	***y***	***z***
Co	0.000000	0.000000	0.000000	Co	0.000000	0.000000	0.000000
N	0.000000	–2.093411	0.214644	N	0.000000	–2.093411	0.214644
N	–0.004781	2.086282	–0.040625	N	–0.004781	2.086282	–0.040625
N	–2.082979	–0.058113	–0.211386	N	–2.082979	–0.058113	–0.211386
N	2.146888	0.057365	–0.086460	N	2.146888	0.057365	–0.086460
O	0.000000	0.000000	1.956371	O	0.000000	0.000000	1.956371
O	–0.037819	–0.170436	–2.138311	O	–0.037819	–0.170436	–2.138311
C	–0.136363	–3.213263	–0.150941	C	–0.136363	–3.213263	–0.150941
C	0.455626	1.026543	2.827232	C	0.455626	1.026543	2.827232
C	–0.549262	–1.018461	–2.989273	C	–0.549262	–1.018461	–2.989273
C	0.096176	3.211534	0.154241	C	0.096176	3.211534	0.154241
C	–3.242701	–0.004047	–0.244611	C	–3.242701	–0.004047	–0.244611
C	3.303249	0.013094	–0.130578	C	3.303249	0.013094	–0.130578
H	–0.702034	–0.376346	2.252827	H	–0.702034	–0.376346	2.252827
H	0.674779	0.131574	–2.537346	H	0.674779	0.131574	–2.537346
H	–0.283128	1.591739	3.068890	H	–0.283128	1.591739	3.068890
H	0.827925	0.632670	3.619581	H	0.827925	0.632670	3.619581
H	1.126062	1.549531	2.383351	H	1.126062	1.549531	2.383351
H	–1.215338	–1.550815	–2.549796	H	–1.215338	–1.550815	–2.549796
H	–0.950773	–0.538913	–3.717633	H	–0.950773	–0.538913	–3.717633
H	0.144988	–1.590084	–3.327958	H	0.144988	–1.590084	–3.327958
H	–5.103699	0.191669	–0.136572	H	–5.103699	0.191669	–0.136572
H	–0.322816	–5.007720	–0.902860	H	–0.322816	–5.007720	–0.902860
H	0.374486	5.082231	0.397901	H	0.374486	5.082231	0.397901
H	5.155369	–0.117158	–0.368388	H	5.155369	–0.117158	–0.368388
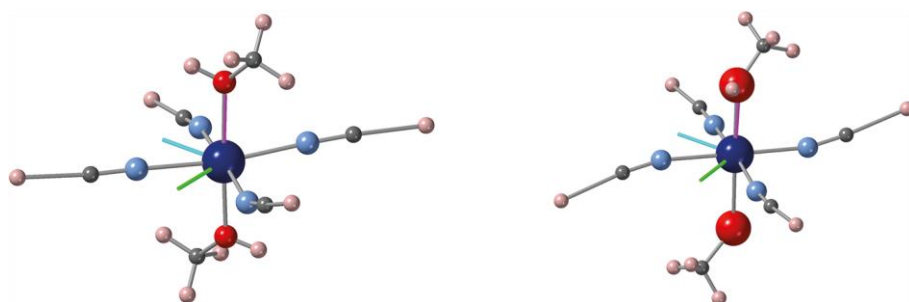
Figure S5. Relative orientation of the experimental coordination sphere geometry of models A (left) and B (right) and the calculated *D* tensor (x = cyan, y = green, z = magenta). Color code: dark blue, cobalt; light blue, nitrogen; red, oxygen; grey, carbon; hydrogen, pink.
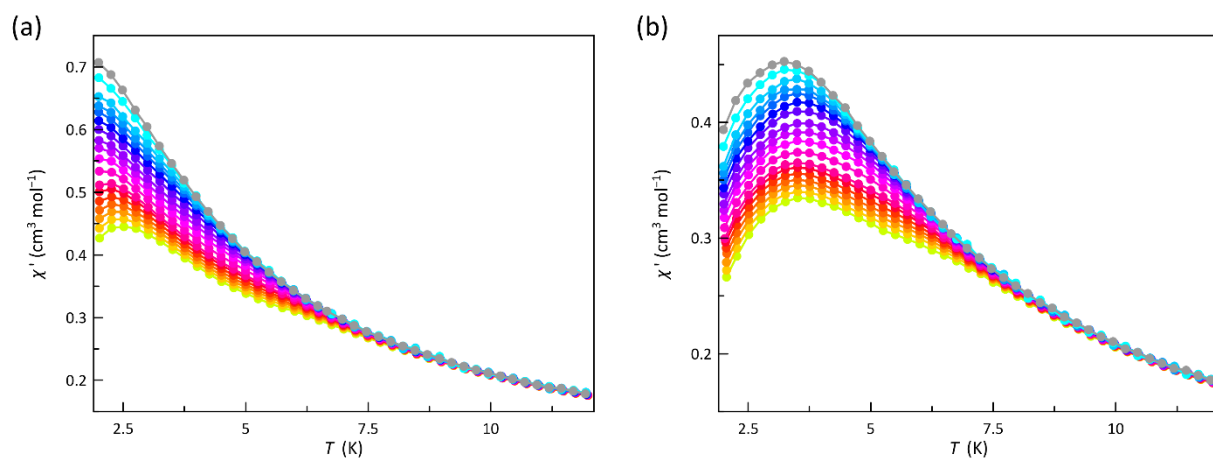
Figure S6. Temperature dependence of χ_M' of **1** under H_{dc} of 2.5 (a) and 5.0 kOe (b) at ±5 Oe oscillating field in the frequency range 0.3–10 kHz (from green to grey). The solid lines are only eye guides.
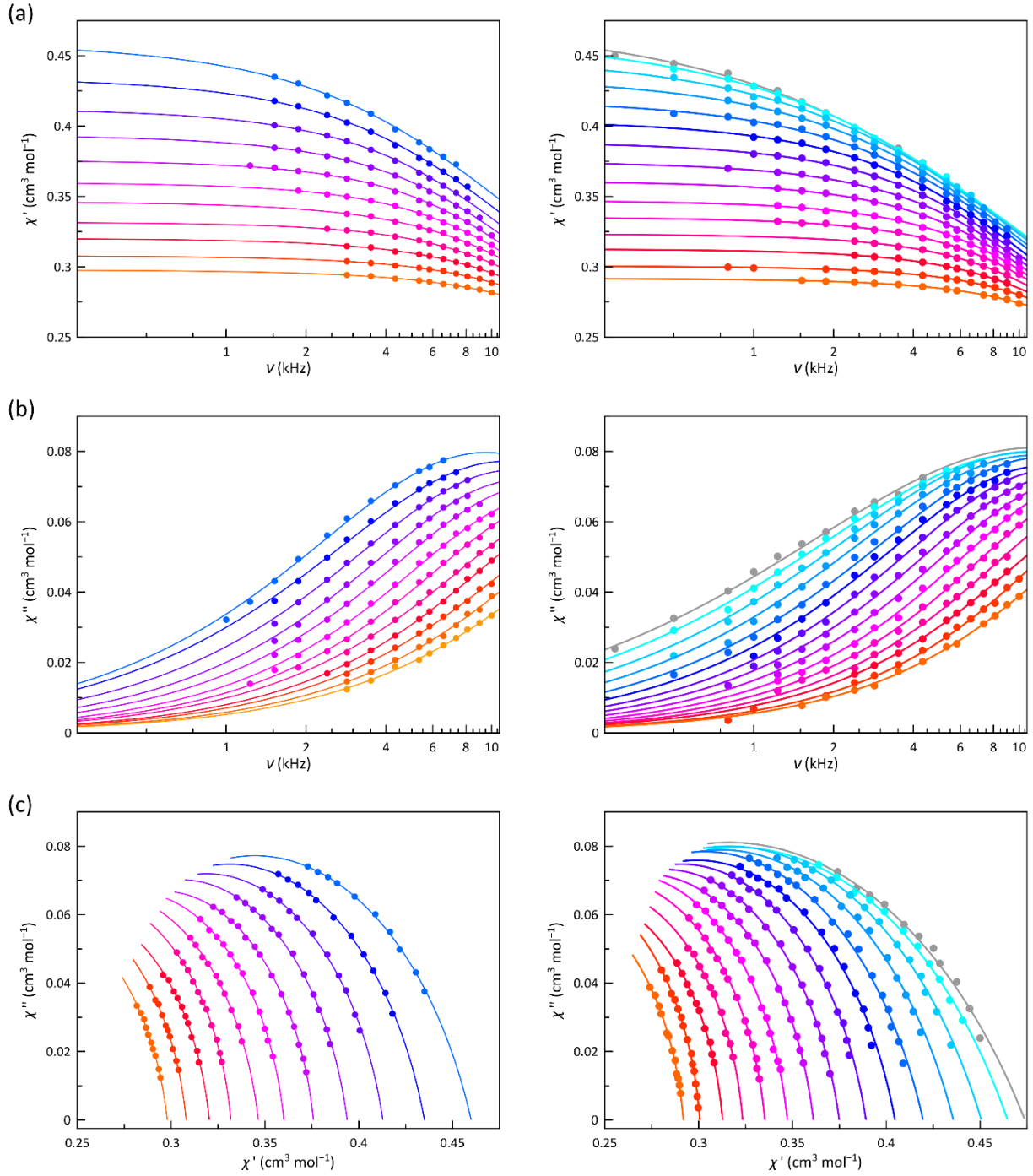
Figure S7. Frequency dependence of χ_M' (a) and χ_M' (b) and Argand plots (c) of **1** under dc magnetic fields of 2.5 (left) and 5.0 kOe (right) at ±0.5 Oe oscillating field in the temperature ranges 4.5–7.0 K and 3.5–7.0 K, respectively (from grey to orange colors).

Table S4. Selected parameters from the least-squares fit of the ac magnetic data of **1**.

H_{dc} (kOe)	τ_{IK}^a (x 10^{-5} s)	C^b ($s^{-1}K^{-n}$)	n^b
2.5	1.69 ± 0.12	0.49 ± 0.05	6.7 ± 0.6
5.0	1.53 ± 0.02	0.59 ± 0.03	6.5 ± 0.2

[a]Coefficient factor for the temperature-independent IK process ($\tau^{-1} = IK$). [b]Coefficient and polynomial factor for the Raman process ($\tau^{-1} = CT^n$).