

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

to

Further synthetic investigation of the general lanthanoid(III) [Ln(III)] / copper(II) / pyridine-2,6-dimethanol / carboxylate reaction system: {Cu^{II}₅Ln^{III}₄} coordination clusters (Ln = Dy, Tb, Ho) and their yttrium(III) analogue

Despina Dermitzaki^{a,b}, Catherine P. Raptopoulou^b, Vassilis Psycharis^b, Albert Escuer^c, Spyros P. Perlepes^{*a,d}, Julia Mayans^{*e} and Theodoros C. Stamatatos^{*a,d}

^a Department of Chemistry, University of Patras, 26504 Patras, Greece.

E-mails: perlepes@upatras.gr, thstama@upatras.gr;

Tel: +30 2610 996730 (S.P.P.), +30 2610 997732 (Th.C.S.)

^b Institute of Nanoscience and Nanotechnology, NCSR “Demokritos”, 15310 Aghia Paraskevi Attikis, Greece.

^c Departament de Química Inorgànica i Orgànica, Secció Inorgànica and Institut de Nanociència i Nanotecnologia (IN2UB), Universitat de Barcelona, Martí i Franquès 1-11, 08028-Barcelona, Spain.

^d Institute of Chemical Engineering Sciences, Foundation for Research and Technology – Hellas (FORTH/ICE – HT), Platani, P.O. Box 1414, 26504, Patras, Greece.

^e Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, Catedrático José Beltrán 2, 46980 Paterna, Spain.

E-mail: julia.mayans@ub.edu

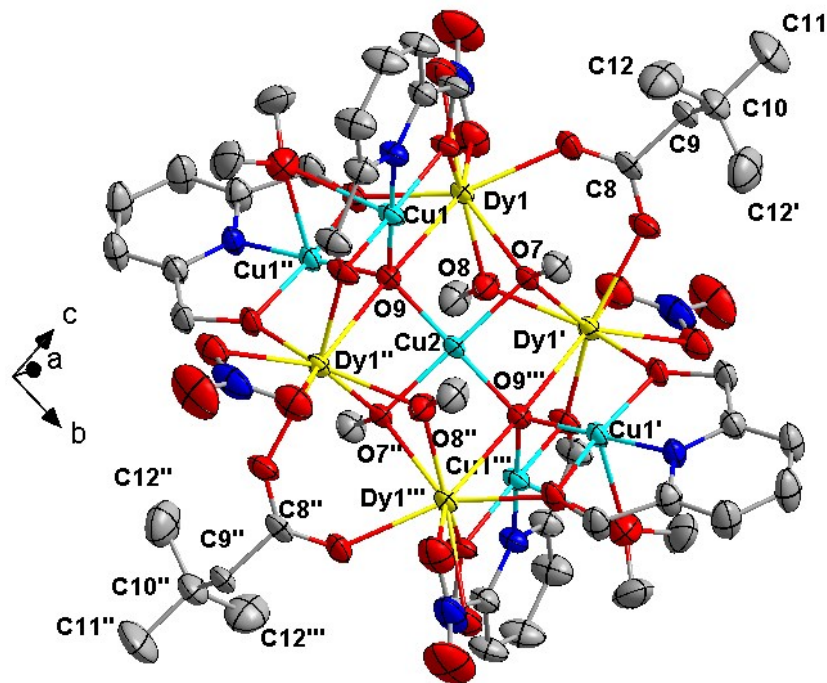


Fig. S1 ORTEP-type plot for the molecule $[\text{Cu}_5\text{Dy}_4\text{O}_2(\text{OMe})_4(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}')_2(\text{pdm})_4(\text{MeOH})_2]$ that is present in the crystal structure of $1 \cdot 4\text{MeCN} \cdot 1.5\text{MeOH}$, with thermal ellipsoids presented at the 50% probability level. Symmetry codes: (') $x, 1-y, z$; (") $2-x, y, -z$; (""') $2-x, 1-y, -z$. The bonds $\text{Cu}2\text{-O}8$ and $\text{Cu}2\text{-O}8''$ have not been drawn (as in Figs. 1 and 2 of the main text) for clarity; they represent weak interactions (see discussion in the main text).

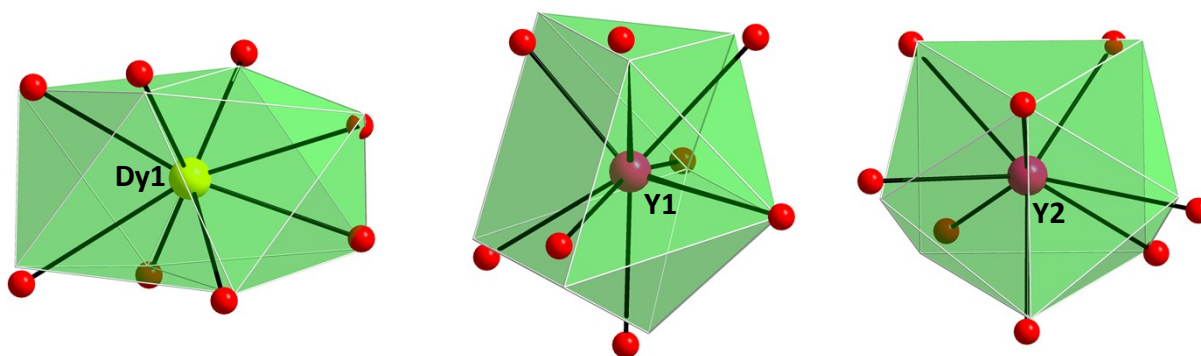


Fig. S2 (Left) The Snub diphenoid polyhedron of the unique Dy^{III} centre in $1 \cdot 4\text{MeCN} \cdot 1.5\text{MeOH}$; (middle, right) The biaugmented trigonal prismatic polyhedra of the two crystallographically independent Y^{III} centres in $2 \cdot 2\text{MeOH}$.

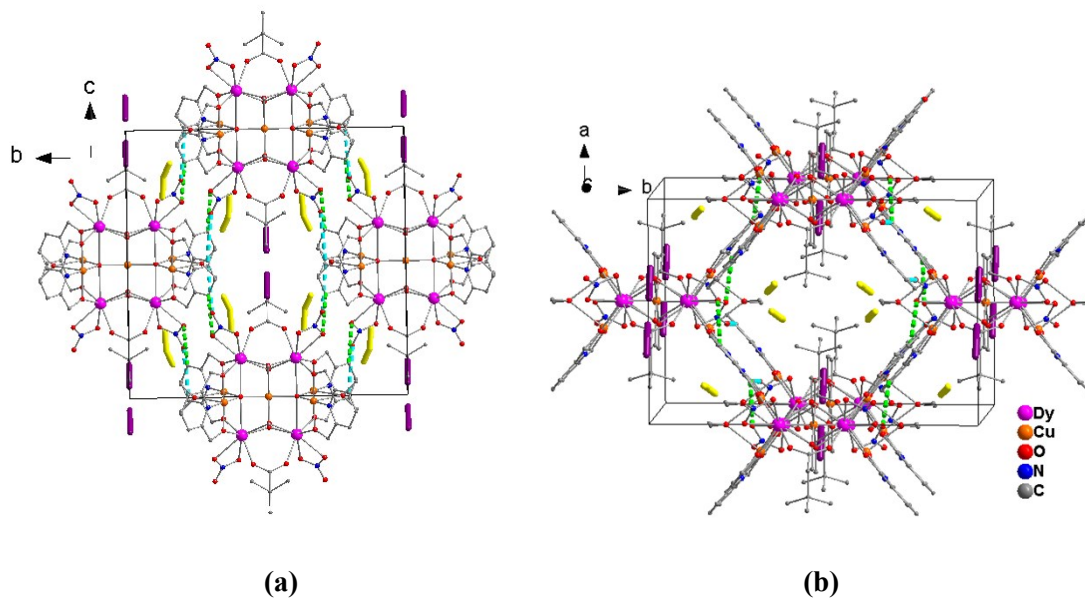


Fig. S3 Views of the crystal structure of compound $1 \cdot 4\text{MeCN} \cdot 1.5\text{MeOH}$ along the a (a) and c (b) crystallographic axes. Yellow and violet thick bars indicate the position of the lattice MeCN molecules. Dashed cyan and light green lines indicate C–H \cdots O hydrogen bonds.

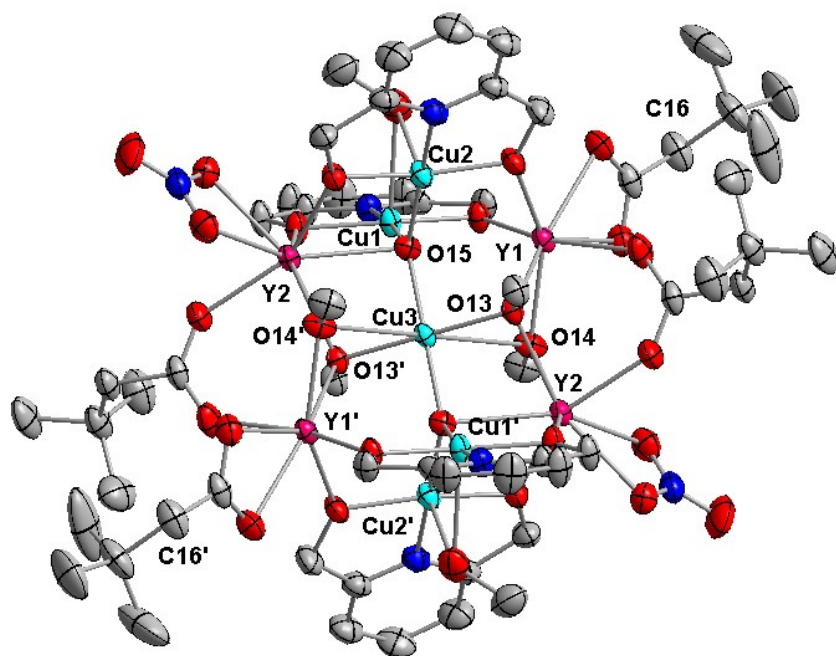


Fig. S4 ORTEP-type plot for the molecule $[\text{Cu}_5\text{Y}_4\text{O}_2(\text{OMe})_4(\text{NO}_3)_2(\text{O}_2\text{CCH}_2\text{Bu}')_4(\text{pdm})_4(\text{MeOH})_2]$ that is present in the crystal structure of $4 \cdot 2\text{MeOH}$, with thermal ellipsoids presented at the 50% probability level. Symmetry codes: (') $2-x, 2-y, 2-z$.

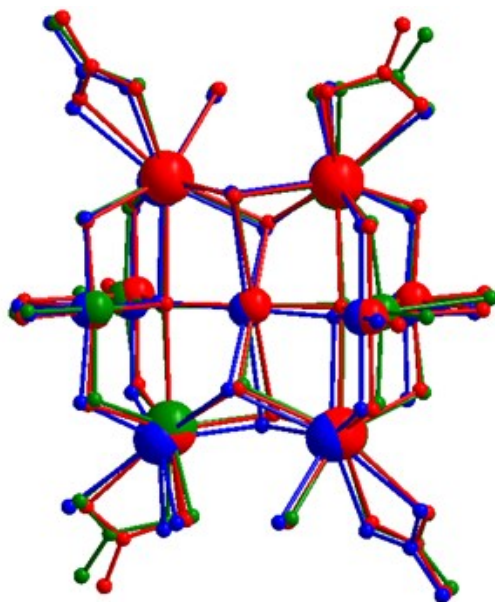


Fig. S7 The $\{Cu_5Ln_4\}$ cluster molecules in complexes $[Cu_5Dy_4O_2(OMe)_4(NO_3)_4(O_2CCH_2Bu^t)_2(pdm)_4(MeOH)_2] \cdot 4MeCN \cdot 1.5MeOH$ (**1**·4MeCN·1.5MeOH) (red), $[Cu_5Y_4O_2(OMe)_4(NO_3)_2(O_2CCH_2Bu^t)_4(pdm)_4(MeOH)_2] \cdot 2MeOH$ (**4**·2MeOH) (blue) and $[Cu_5Dy_4O_2(OMe)_4(NO_3)_4(O_2CBu^t)_2(Htea)_4] \cdot 2MeOH \cdot 2Et_2O$ (green) [ref. 74 of the main text].

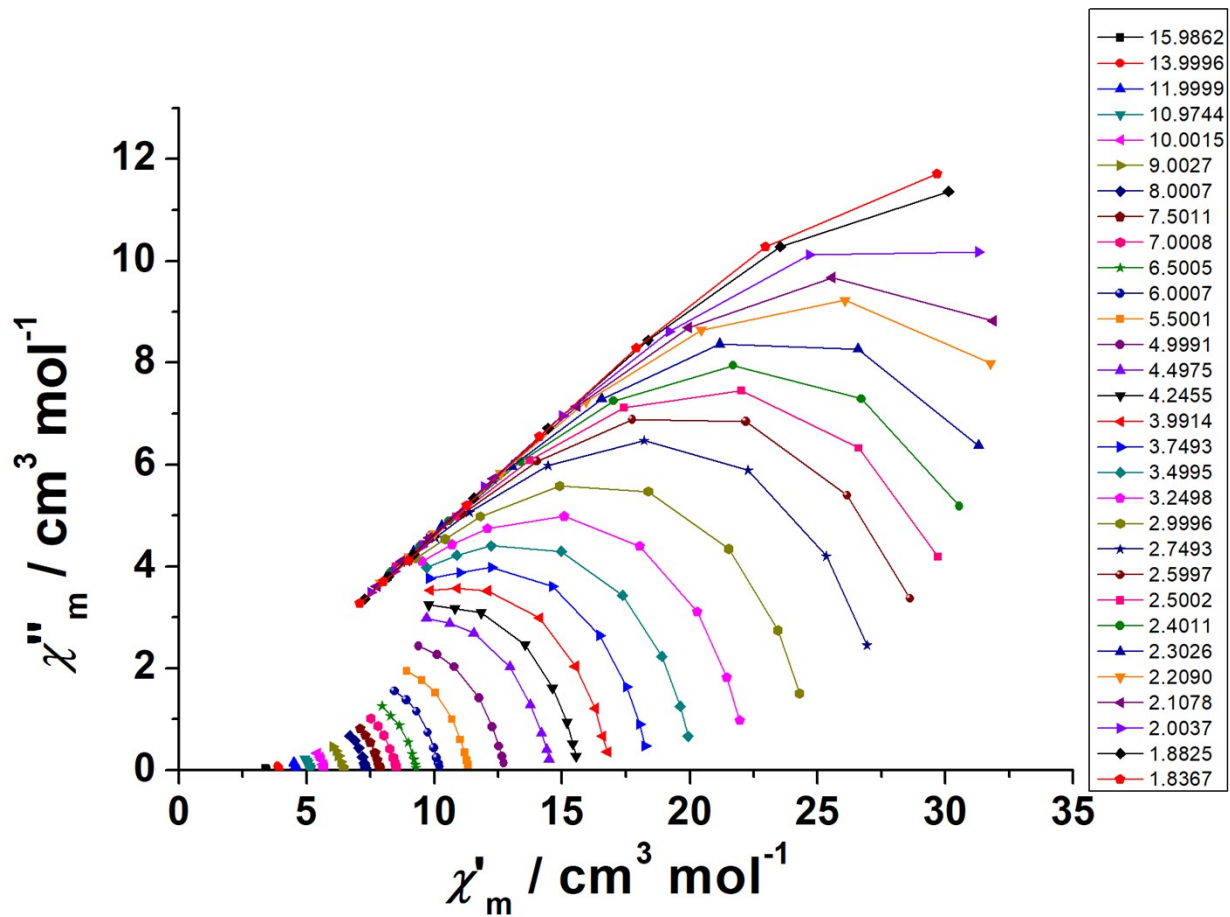


Fig. S8 Argand (Cole-Cole) plots for **1** at zero dc field at the indicated temperatures. The solid lines are guides for the eye.

Table S1 Crystallographic data for compounds **1**·4MeCN·1.5MeOH and **4**·2MeOH

Parameter	1 ·2.8MeCN	4 ·2MeOH
Formula	C _{55.5} H ₈₈ Cu ₅ Dy ₄ N ₁₂ O _{33.5}	C ₆₀ H ₁₀₀ Cu ₅ Y ₄ N ₆ O ₃₂
F_w	2427.07	2090.79
Crystal system	Monoclinic	Triclinic
Space group	$I2/m$	$P\bar{1}$
$a / \text{Å}$	13.1964(4)	11.8882(16)
$b / \text{Å}$	18.9068(6)	13.9025(19)
$c / \text{Å}$	18.3821(6)	14.6268(19)
$\alpha / ^\circ$	90.0	109.848(4)
$\beta / ^\circ$	98.374(2)	103.739(4)
$\gamma / ^\circ$	90.0	102.604(4)
$V / \text{Å}^3$	4537.5(2)	2087.3(5)
Z	2	1
$T / ^\circ\text{C}$	-113	-113
Radiation / μ (mm ⁻¹)	Mo K α / 4.475	Mo K α / 4.073
$\rho_{\text{calcd}} / \text{g cm}^{-3}$	1.775	1.663
Reflections collected/unique (R_{int})	28462/5094 (0.0509)	37354/9087 (0.0540)
Reflections with $I > 2\sigma(I)$	4422	7043
No. of parameters	265	564
$R_1^a [I > 2\sigma(I)]$, $wR_2^b [I > 2\sigma(I)]$	0.0352, 0.0906	0.0350, 0.0704
R_1^a (all data), wR_2^b (all data)	0.0418, 0.0953	0.0548, 0.0776
$(\Delta/\sigma)_{\text{max}}$	0.008	0.002
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.284 / -1.529	0.498 / -0.475
CCDC number	2038607	2038608

^a $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma(|F_o|)$. ^b $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2 F_c^2] / 3$. $a = 0.0448$ and $b = 28.4514$ for **1**·4MeCN·1.5MeOH; $a = 0.0315$ and $b = 1.2328$ for **4**·2MeOH.

SHORT IR DISCUSSION

The IR spectra (recorded in KBr pellets) of vacuum-dried samples of **1** – **4** exhibit a medium-intensity broad band at $\sim 3425\text{ cm}^{-1}$ assignable to $\nu(\text{OH})_{\text{coord. MeOH}}$.¹ The in-plane and out-of-plane deformation modes of the 2,6-pyridyl ring of pdm^{2-} appear at ~ 660 and $\sim 430\text{ cm}^{-1}$, respectively; the higher wavenumbers of these bands compared with the free ligand suggest the involvement of the ring-N atom in coordination.^{1,2} The $1655 - 1250\text{ cm}^{-1}$ region is almost identical in the spectra of **1** – **3**. Many bands appear due to contributions – among others – from the stretching vibrations of the 2,6-pyridyl ring, and the coordinated carboxylate and nitrate groups. As overlap is possible, several bands most probably do not represent pure vibrations, and this renders accurate assignments and studies of the coordination shifts tentative. The bands at ~ 1650 and $\sim 1410\text{ cm}^{-1}$ are assigned³ to the $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ vibrations, respectively, of the $\text{Bu}'\text{CH}_2\text{CO}_2^-$ ligands; their difference Δ , where $\Delta = \nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2)$, is rather small ($\sim 240\text{ cm}^{-1}$), as expected for the bidentate bridging mode of the carboxylate ligation.^{3,4} The bands at ~ 1470 and $\sim 1265\text{ cm}^{-1}$ are assigned⁵ to the $\nu_1(A_1)[\nu(\text{N}=\text{O})]$ and $\nu_5(B_2)[\nu_{\text{as}}(\text{NO}_2)]$ vibrational modes, respectively, of the coordinated nitrate group. The separation of these two, highest-frequency stretching bands is large ($>200\text{ cm}^{-1}$), indicating the bidentate character of the nitrate ligands.⁵ The spectra also exhibit a strong band at 1384 cm^{-1} , characteristic of the $\nu_3(E')[\nu_{\text{d}}(\text{NO})]$ mode of the planar D_{3h} ionic nitrate;⁵ such a nitrate is absent in the structures of the complexes (*vide infra*). The presence of this band suggests that a certain amount of nitrate ligands is replaced by bromides that exist in large excess in the spectroscopic KBr matrix, thus generating ionic nitrates in the form of KNO_3 ; this exchange, well documented in the literature,⁶ is facilitated by the pressure used for the preparation of the KBr discs. The $1650 - 1250\text{ cm}^{-1}$ region is slightly different in the spectrum of **4**, suggesting a different ligation of the carboxylate and/or nitrate groups for this complex; this difference has been confirmed by the single-crystal X-ray structure of the $\{\text{Cu}_5\text{Y}_4\}$ complex (*vide infra*).

- ¹ D. Dermitzaki, C.P. Raptopoulou, V. Psycharis, A. Escuer, S.P. Perlepes and T.C. Stamatatos, *Inorg. Chem.*, 2015, **54**, 7555.
- ² Y.T. Yilmaz, S. Hamamci and C. Thöne, *Polyhedron*, 2004, **23**, 841.
- ³ G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.
- ⁴ D. Martinez, M. Motevalli and M. Watkinson, *Dalton Trans.*, 2010, **39**, 446.
- ⁵ K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn, Wiley, New York, 1986, pp. 254-257.
- ⁶ G.J. Kleywegt, W.G.R. Wiesmeijer, G.J. van Driel, W.L. Driessen, J. Reedijk and J.H. Noordik, *J. Chem. Soc. Dalton Trans.*, 1985, 2177.