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A new family of high nuclearity Co^{II}/Dy^{III} coordination clusters possessing robust and unseen topologies†

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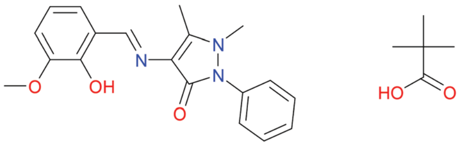
Mixing $Co(NO_3)_2\cdot 6H_2O/Dy(NO_3)_3\cdot 6H_2O$/(*E*)-4-(2-hydroxy-3-methoxybenzylideneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (HL)/pivalic acid/Et_3N in various solvents results in the synthesis of seven compounds formulated as $[Co^{II}_2Dy^{III}_2(\mu_3\text{-}MeO)_2(L)_2(piv)_4(NO_3)_2]$ (**3**), $[Co^{II}Dy^{III}_3(\mu_3\text{-}MeO)_2(\mu_2\text{-}MeO)_2(L)_2(piv)_2(NO_3)_3]\cdot 2(CH_3OH)$ (**4**$\cdot 2CH_3OH$), $2[Co^{II}_4Dy^{III}_4(\mu_2\text{-}O)_2(\mu_3\text{-}OH)_4(L)_4(piv)_8][Co^{II}_2Dy^{III}_5(\mu_3\text{-}OH)_6(L)_2(\text{-}piv)_8(NO_3)_4]$ (**5**), $[Co^{II}_4Dy^{III}_4(\mu_2\text{-}O)_2(\mu_3\text{-}OH)_4(L)_4(piv)_8]\cdot 2(CH_3CN)$ (**6**$\cdot 2CH_3CN$), $[Co^{II}_2Dy^{III}_5(\mu_3\text{-}OH)_6(L)_2(\text{-}piv)_8(NO_3)_4]\cdot 4(CH_3CN)$ (**7**$\cdot 4CH_3CN$), $[Co^{II}_2Dy^{III}_2(\mu_3\text{-}OH)_2(L)_2(piv)_2(NO_3)_2(EtOH)_2(H_2O)_2](NO_3)_2\cdot(EtOH)$ (**8**$\cdot$EtOH) and $[Co^{II}_4Dy^{III}_4(\mu_2\text{-}O)_2(\mu_3\text{-}OH)_4(L)_4(piv)_8]$ (**9**) with robust and unseen topologies. These show that the temperature and reaction time influence the formation of the final product. Preliminary magnetic studies, performed for **6** and **7** in the temperature range 2–300 K, are indicative of Single Molecule Magnet (SMM) behaviour. Moreover, analysis of the catalytic properties of compound **3** as an efficient catalyst for the synthesis of *trans*-4,5-diaminocyclopent-2-enones from 2-furaldehyde and primary amines has been carried out.

Introduction

In recent years, 3d/4f coordination cluster chemistry has received attention due to the fascinating structures[1–5] and properties that these materials display.[6–9] The simple preparative procedure and the wide range of 3d, 4f elements and organic ligands that can be used have led to numerous compounds with unprecedented structures.[10] The high coordination numbers that lanthanides favour make prediction and description of the final product difficult. Recognizing the importance of topology in the development of coordination polymer chemistry,[11] and aiming to create order in the fast-expanding group of polynuclear coordination clusters (CCs), we have developed a methodology which simplifies the description of the complicated structures of such species.[12,13] This methodology classifies[14,15] and compares polynuclear CCs of defined nuclearity and topology[14] and allows a graphical search for structural motifs.[16]

We recently employed (*E*)-4-(2-hydroxy-3-methoxybenzylideneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (HL, (Scheme 1, left)) in Co/Ln chemistry, in the absence of a co-ligand to give two isoskeletal $Co^{II}_3Dy^{III}_4$ CCs formulated as $[Co^{II}_3Dy^{III}_4\text{-}(\mu_3\text{-}OH)_6L_6(CF_3SO_3)](ClO_4)_5$ (**1**) and $[Co^{II}_3Dy^{III}_4(\mu_3\text{-}OH)_6L_6\text{-}(CF_3SO_3)](ClO_4)_3(CF_3SO_3)_2$ (**2**) possessing a disk-like or **3,6M7-1** topology, previously unseen in Co/Ln chemistry and exhibiting interesting magnetic properties.[17] The two different coordination pockets, the limited degree of flexibility of the ligand, the unusual Co/Dy topology and the higher nuclearity afforded in comparison with compounds containing similar ligands,[18] lead us to explore the coordination chemistry of HL in more detail and to undertake a systematic investigation.

Since pivalic acid (pivH) has been shown to be an excellent co-ligand, preventing extensive hydrolysis of the metal centres, for the synthesis of 3d/4f polynuclear CCs,[19–25] we decided to



Scheme 1 The protonated forms of (*E*)-4-(2-hydroxy-3-methoxybenzylideneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (HL) ligand (left) and Pivalic acid (right) used in this study.

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incorporate it in the reaction system that afforded the two isoskeletal $Co^{II}_3Dy^{III}_4$ CCs (**1** and **2**), resulting in the synthesis of seven new compounds formulated as $[Co^{II}_2Dy^{III}_2(\mu_3\text{-MeO})_2(L)_2(piv)_4(NO_3)_2]$ (**3**), $[Co^{II}Dy^{III}_3(\mu_3\text{-MeO})_2(\mu_2\text{-MeO})_2(L)_2(piv)_2(NO_3)_3]\cdot 2(CH_3OH)$ ($\mathbf{4}\cdot 2CH_3OH$), $2[Co^{II}_4Dy^{III}_4(\mu_2\text{-O})_2(\mu_3\text{-OH})_4(L)_4(piv)_8]$-$[Co^{II}_2Dy^{III}_5(\mu_3\text{-OH})_6(L)_2(piv)_8(NO_3)_4]$ (**5**), $[Co^{II}_4Dy^{III}_4(\mu_2\text{-O})_2(\mu_3\text{-OH})_4(L)_4(piv)_8]\cdot 2(CH_3CN)$ ($\mathbf{6}\cdot 2CH_3CN$), $[Co^{II}_2Dy^{III}_5(\mu_3\text{-OH})_6(L)_2(piv)_8(NO_3)_4]\cdot 4(CH_3CN)$ ($\mathbf{7}\cdot 4CH_3CN$), $[Co^{II}_2Dy^{III}_2(\mu_3\text{-OH})_2(L)_2(piv)_2(NO_3)_2(EtOH)_2(H_2O)_2](NO_3)_2\cdot(EtOH)$ ($\mathbf{8}\cdot EtOH$) and $[Co^{II}_4Dy^{III}_4(\mu_2\text{-O})_2(\mu_3\text{-OH})_4(L)_4(piv)_8]$ (**9**) with robust and unprecedented topologies. These show that the temperature and reaction time influence the formation of the final product. Preliminary magnetic studies, performed for **6** and **7** in the temperature range 2–300 K, are indicative of Single Molecule Magnet (SMM) behaviour. Moreover, compound **3** has been tested as an efficient catalyst for the synthesis of *trans*-4,5-diaminocyclopent-2-enones from 2-furaldehyde and primary amines.

Experimental

Materials and methods

Materials. Chemicals (reagent grade) were purchased from Sigma Aldrich and Alfa Aesar. All experiments were performed under aerobic conditions using materials and solvents as received.

Instrumentation. NMR spectra were recorded on a Varian VNMRS solution-state spectrometer at 500 MHz at 30 °C using residual isotopic solvent (DMSO, $\delta_H = 2.50$ ppm) as an internal reference. Chemical shifts are quoted in ppm. Coupling constants (J) are recorded in Hz. IR spectra of the samples were recorded over the range of 4000–650 cm^{-1} on a Perkin Elmer Spectrum One FT-IR spectrometer fitted with a UATR polarization accessory. EI-MS was performed on a VG Autospec Fissions instrument (EI at 70 eV).

Synthetic procedures

Ligand synthesis. The synthesis of HL has been carried out according to the reported synthetic procedure.[17]

Synthesis of $[Co^{II}_2Dy^{III}_2(\mu_3\text{-MeO})_2(L)_2(piv)_4(NO_3)_2]$ *(3).* 0.075 g (0.22 mmol) of L and 0.036 g (0.35 mmol) of pivalic acid were added to 20 ml of MeOH and stirred. To this 118 μl (0.84 mmol) of 99% NEt_3 were added and the resulting mixture was brought to 40 °C and stirred for 10 minutes. To this 0.068 g (0.23 mmol) of $Co^{II}(NO_3)_2\cdot 6H_2O$ and 0.104 g (0.23 mmol) of $Dy^{III}(NO_3)_3\cdot 5H_2O$ were added and the resulting mixture was stirred at 40 °C for a further hour. This was then filtered and left undisturbed for slow evaporation; orange diamond shaped plate-like crystals of **3** formed 7 days later. Yield: 35.5 mg (18.3% based on Co). Selected IR peaks (cm^{-1}): 2960.53 (br), 1608.15 (s), 1467.22 (s), 1312.43 (m), 1215.08 (m), 736.21 (m). Attempts to characterize, *via* X-ray crystallography, the residue on the filter were not successful.

Synthesis of $[Co^{II}Dy^{III}_3(\mu_3\text{-MeO})_2(\mu_2\text{-MeO})_2(L)_2(piv)_2(NO_3)_3]\cdot 2(CH_3OH)$ *(4).* 0.075 g (0.22 mmol) of L and 0.036 g (0.35 mmol) of pivalic acid were added to 20 ml of MeOH and stirred. To this 118 μl (0.84 mmol) of 99% NEt_3 were added and the resulting mixture was brought to reflux and stirred for 10 minutes. To this 0.068 g (0.23 mmol) of $Co^{II}(NO_3)_2\cdot 6H_2O$ and 0.130 g (0.29 mmol) of $Dy^{III}(NO_3)_3\cdot 5H_2O$ were added and the resulting mixture was refluxed for an hour. This was then filtered and left undisturbed for slow evaporation; orange needle like crystals of **4** formed within 48 hours. Yield: 23 mg (16.9% based on Dy). Selected IR peaks (cm^{-1}): 2955.32 (br), 1595.00 (m), 1551.31 (m), 1459.74 (s), 1420.58 (s), 1300.85 (s), 1211.06 (s), 1014.61 (m), 747.41 (m), 700.82 (m).

Synthesis of $2[Co^{II}_4Dy^{III}_4(\mu_2\text{-O})_2(\mu_3\text{-OH})_4(L)_4(piv)_8][Co^{II}_2Dy^{III}_5(\mu_3\text{-OH})_6(L)_2(piv)_8(NO_3)_4]$ *(5).* 0.075 g (0.22 mmol) of L and 0.036 g (0.35 mmol) of pivalic acid were added to 20 ml of MeCN and stirred. To this 118 μl (0.84 mmol) of 99% NEt_3 were added and the resulting mixture was brought to 40 °C and stirred for 10 minutes. To this 0.068 g (0.23 mmol) of $Co^{II}(NO_3)_2\cdot 6H_2O$ and 0.104 g (0.23 mmol) of $Dy^{III}(NO_3)_3\cdot 5H_2O$ were added and the resulting mixture was stirred at 40 °C for a further hour. This was then filtered and left undisturbed for slow evaporation. Crystals of **5** were formed within 72 hours. Yield: 28 mg (17% based on Dy).

Synthesis of $[Co^{II}_4Dy^{III}_4(\mu_2\text{-O})_2(\mu_3\text{-OH})_4(L)_4(piv)_8]\cdot 2(CH_3CN)$ *(6).* 0.075 g (0.22 mmol) of L and 0.036 g (0.35 mmol) of pivalic acid were added to 20 ml of MeCN and stirred. To this 118 μl (0.84 mmol) of 99% NEt_3 were added and the resulting mixture was brought to reflux and stirred for 10 minutes. To this 0.068 g (0.23 mmol) of $Co^{II}(NO_3)_2\cdot 6H_2O$ and 0.104 g (0.23 mmol) of $Dy^{III}(NO_3)_3\cdot 5H_2O$ were added and the resulting mixture was refluxed for a further hour. This was then filtered and left undisturbed for slow evaporation; red hexagonal plate like crystals of **6** formed within 48 hours. Yield: 18.2 mg (10.4% based on Co). Selected IR peaks (cm^{-1}): 2958.46 (br), 1603.96 (s), 1544.31 (s), 1419.35 (s), 1219.56 (s), 1104.31 (m), 967.74 (m), 742.29 (m), 705.04 (m).

Synthesis of $[Co^{II}_2Dy^{III}_5(\mu_3\text{-OH})_6(L)_2(piv)_8(NO_3)_4]\cdot 4(CH_3CN)$ *(7).* 0.075 g (0.22 mmol) of L and 0.036 g (0.35 mmol) of pivalic acid were added to 20 ml of MeCN and stirred. To this 118 μl (0.84 mmol) of 99% NEt_3 were added and the resulting mixture was brought to reflux and stirred for 10 minutes. To this 0.068 g (0.23 mmol) of $Co^{II}(NO_3)_2\cdot 6H_2O$ and 0.104 g (0.23 mmol) of $Dy^{III}(NO_3)_3\cdot 5H_2O$ were added and the resulting mixture was refluxed for a further 24 hours. This was then filtered and left undisturbed for slow evaporation; orange rectangular plate like crystals of **7** formed within 72 hours. Yield: 16 mg (13.0% based on Dy). Selected IR peaks (cm^{-1}): 2958.26 (m, br), 1605.7 (m), 1556.13 (s), 1485.01 (s), 1423.04 (s), 1221.42 (m), 1033.26 (m).

Synthesis of $[Co^{II}_2Dy^{III}_2(\mu_3\text{-OH})_2(L)_2(piv)_2(NO_3)_2(EtOH)_2(H_2O)_2](NO_3)_2(EtOH)$ *(8).* 0.075 g (0.22 mmol) of L and 0.036 g (0.35 mmol) of pivalic acid were added to 20 ml of EtOH and stirred. To this 118 μl (0.84 mmol) of 99% NEt_3 were added and the resulting mixture was brought to reflux and stirred for 10 minutes. To this 0.068 g (0.23 mmol) of $Co^{II}(NO_3)_2\cdot 6H_2O$ and 0.104 g (0.23 mmol) of $Dy^{III}(NO_3)_3\cdot 5H_2O$ were added and the resulting mixture was refluxed for a further hour. This was then filtered and left undisturbed for slow evaporation; large red crystals of **8** formed within 48 hours. Yield: 91 mg (46.9% based on Co). Selected IR peaks (cm^{-1}): 3242.7 (br), 2971.00 (w), 1483.94 (s), 1454.42 (s), 1420.39 (s), 1300.92 (s), 1036.49 (s), 961.76 (m), 745.43 (s), 706.18 (m).

Synthesis of $[Co^{II}_4Dy^{III}_4(\mu_2\text{-}O)_2(\mu_3\text{-}OH)_4(L)_4(piv)_8]$ *(9).* 0.075 g (0.22 mmol) of L and 0.036 g (0.35 mmol) of pivalic acid were added to 20 ml of EtOH and stirred. To this 118 µl (0.84 mmol) of 99% NEt_3 were added and the resulting mixture was brought to reflux and stirred for 10 minutes. To this 0.068 g (0.23 mmol) of $Co^{II}(NO_3)_2{\cdot}6H_2O$ and 0.104 g (0.23 mmol) of $Dy^{III}(NO_3)_3{\cdot}5H_2O$ were added and the resulting mixture was refluxed for a further 24 hours. This was then filtered and left undisturbed for slow evaporation; red hexagonal plate like crystals of **9** formed within 48 hours. Yield: 24.5 mg (14.0% based on Co). Selected IR peaks (cm^{-1}): 2958.46 (br), 1603.96 (s), 1544.31 (s), 1419.35 (s), 1219.56 (s), 1104.31 (m), 967.74 (m), 742.29 (m), 705.04 (m).

Conversion of **8** to **6**. 10 mg (0.00623 mmol) of **8** was added along with 1.27 mg (0.01246 mmol) of pivalic acid to 5 ml MeCN. To this 0.86 µl (0.00623 mmol) of 99% NEt_3 were added and the resulting mixture was stirred and refluxed for 24 hours. Crystals of **6** were formed within 72 hours. Conversion of **8** to **9**. 10 mg (0.00623 mmol) of **8** was added along with 1.27 mg (0.01246 mmol) of pivalic acid to 5 ml EtOH. To this 0.86 µl (0.00623 mmol) of 99% NEt_3 were added and the resulting mixture was stirred and refluxed for 24 hours. Crystals of **9** were formed within 72 hours.

Magnetic studies. Magnetic susceptibility measurements were carried out on polycrystalline samples with a MPMS5 Quantum Design susceptometer working in the range 30–300 K under an external magnetic field of 0.3 T and under a field of 0.03 T in the 30–2 K range to avoid saturation effects. Diamagnetic corrections were estimated from Pascal Tables.

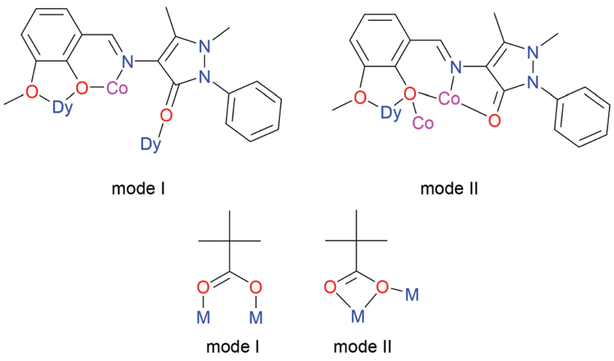
Crystallography. Data for **4** and **8** were collected (ω-scans) at the University of Sussex using an Agilent Xcalibur Eos Gemini Ultra diffractometer with a CCD plate detector under a flow of nitrogen gas at 173(2) K using Mo Kα radiation (λ = 0.71073 Å). CRYSALIS CCD and RED software were used respectively for data collection and processing. Reflection intensities were corrected for absorption by the multi-scan method. Data for **3**, **5**, **6**, **7**, **8′** and **9** were collected at the National Crystallography Service, University of Southampton[26] using a Rigaku Saturn 724+ area detector mounted at the window of an FR-E+ rotating anode generator with a Mo anode (λ = 0.71075 Å) under a flow of nitrogen gas at 100(2) K. All structures were determined using Olex2,[27] solved using either Superflip[28] or SHELXT[29,30] and refined with SHELXL-2014.[31] All non-H atoms were refined with anisotropic thermal parameters, and H-atoms were introduced at calculated positions and allowed to ride on their carrier atoms. Geometric/crystallographic calculations were performed using PLATON,[32] Olex2,[27] and WINGX[29] packages; graphics were prepared with Crystal Maker.[33] Crystallographic details for **3–9** are given in Table S1.†

Results and discussion

Some general observations for all compounds are: (a) except **4**, each L^{-} is chelated to a Co^{II} centre, forming a cationic metallo-ligand, (CoL)$^{+}$, which in turn is linked to other metal centres, (b) L^{-} is coordinated to three metal centres exhibiting two different coordination modes (modes I and II, Scheme 2, above), (c) two coordination modes can be found for the co-ligand (Scheme 2, below), (d) Co^{II} centres are six coordinated in an essentially regular octahedral coordination and (e) the coordination spheres of the Dy centres are completed by the carboxylate and the nitrate groups.

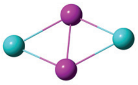
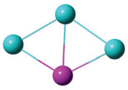
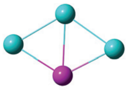
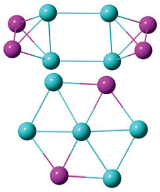
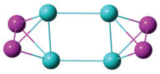
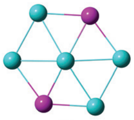
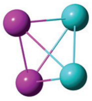
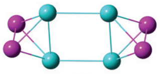
By changing the reaction conditions that afforded **1**,[17] introducing pivalic acid as a co-ligand, and heating at 40 °C for one hour (Table 1, entry 1), we obtained orange diamond-shaped crystals of compound **3** (Fig. 1a). The structure, confirmed by X-ray studies,[26] possesses the well-known defect dicubane[34] or, according to our nomenclature, **2,3M4-1**[13] topology. The coordination number of the two Dy^{III} ions is 8. Using Shape software,[35] the geometry of Dy(1) can be best described as biaugmented trigonal prism or square antiprism [$S(P)$ values 1.767 and 1.968, respectively] and of Dy(2) as biaugmented trigonal prism [$S(P)$ = 2.372].

The orange needles obtained under reflux (Table 1, entry 2) were found to be **4**·2(CH$_3$OH) (Fig. 1b), also possessing the defect dicubane or **2,3M4-1** topology. In this compound, two L^{-} are chelated to a Co^{II} centre, forming a neutral metallo-ligand, (CoL$_2$), which in turn is linked to the Dy^{III} centres. The coordination number of all Dy^{III} ions is 8. Using Shape software,[35] the geometry of Dy(1) can be best described as intermediate between heptagonal pyramid and Johnson elongated triangular bipyramid, and the geometry of Dy(2) can be best described as an intermediate of Johnson gyrobifastigium,[36] biaugmented trigonal prism and elongated trigonal bipyramid. The lattice methanol is hydrogen bonded to the chelated nitrate group of Dy(2). Reaction for a longer time (Table 1, entry 3) again gave **4**, confirmed by a unit cell check. To the best of our knowledge, such a defect dicubane Co^{II}Dy$^{III}_3$ topology has not previously been reported. In both **3** and **4**, MeO



Scheme 2 (Above) The two coordination modes of the ligand. Mode I is seen in compounds 3, 4, 5 and 7, mode II is seen in 5, 6, 8, 8′ and 9. (Below) The two coordination modes seen in 3–9 for the pivalate anion.

Table 1 A summary of the reaction conditions for the formation of **3–9**

Entry	Solvent	Temperature/time (h)	Topology	Product
1	MeOH	40 °C/1	**2,3M4-1**	 **3**
2	MeOH	Reflux (65 °C)/1	**2,3M4-1**	 **4**
3	MeOH	Reflux (65 °C)/24	**2,3M4-1**	 **4**
4	MeCN	40 °C/1	**2 (3,4M8-3) + 3,6M7-1**	 **5**
5	MeCN	Reflux (82 °C)/1	**3,4M8-3**	 **6**
6	MeCN	Reflux (82 °C)/24	**3,6M7-1**	 **7**
7	EtOH	40 °C/1	**3M4-1**	 **8**
8	EtOH	Reflux (79 °C)/1	**3M4-1**	 **8'**
9	EtOH	Reflux (79 °C)/24	**3,4M8-3**	 **9**

groups, arising from solvent deprotonation, bridge the metal centres in a μ_2- or μ_3-fashion and, the structure is unchanged, even after prolonged heating under reflux.

As the complexes required bridging MeO groups to give a defect dicubane geometry it would be reasonable to suggest that a non-coordinating solvent may result in different topologies. Indeed, repetition of the reaction that afforded **3** in CH_3CN instead of CH_3OH (Table 1, entry 4), results in orange hexagonal crystals of **5** (Fig. 1c), the lattice of which contains two octanuclear and one heptanuclear Co^{II}/Dy^{III} unit. The octanuclear one can be considered as two Co$_2^{II}$Dy$_2^{III}$ cubanes joined by two oxo bridges, and bridged by four pivalates, possessing a **3,4M8-3** topology (Table 1, entry 4) and the heptanuclear fragment possesses a disk-like or **3,6M7-1** topology. According to our survey, both topologies are unprecedented in Co/Ln chemistry, and mixed nuclearity CCs are very rare in coordination chemistry as a whole.[37] The unusual **3,4M8-3** topology can be found in compounds containing solely Fe,[38,39] Zn[40] and Dy[41] but not in mixed metal species. Additionally, the **3,6M7-1** topology has been seen in mixed valence Co$^{II/III}$[42–44] and Dy^{III}[45] compounds, in a series of Mn$_3^{II}$Ln$_4^{III}$,[46] and Cu$_5^{II}$Ln$_2^{III}$[47] compounds, as well in the heptanuclear Mn$_6^{IV}$Ce^{IV},[48,49] Cu$_6^{II}$Pr^{III}[50] and Co$_3^{II}$Dy$_4^{III}$[17] compounds. Moreover, the existence of two bridging μ_2-O atoms is very rare in lanthanide chemistry. Only eight compounds are known with double bridging oxygen atoms; the Dy–O and the O–Dy–O values are in line with the previous reported examples.[51,52] Triply bridging hydroxyl groups further support the formation of both species. In the

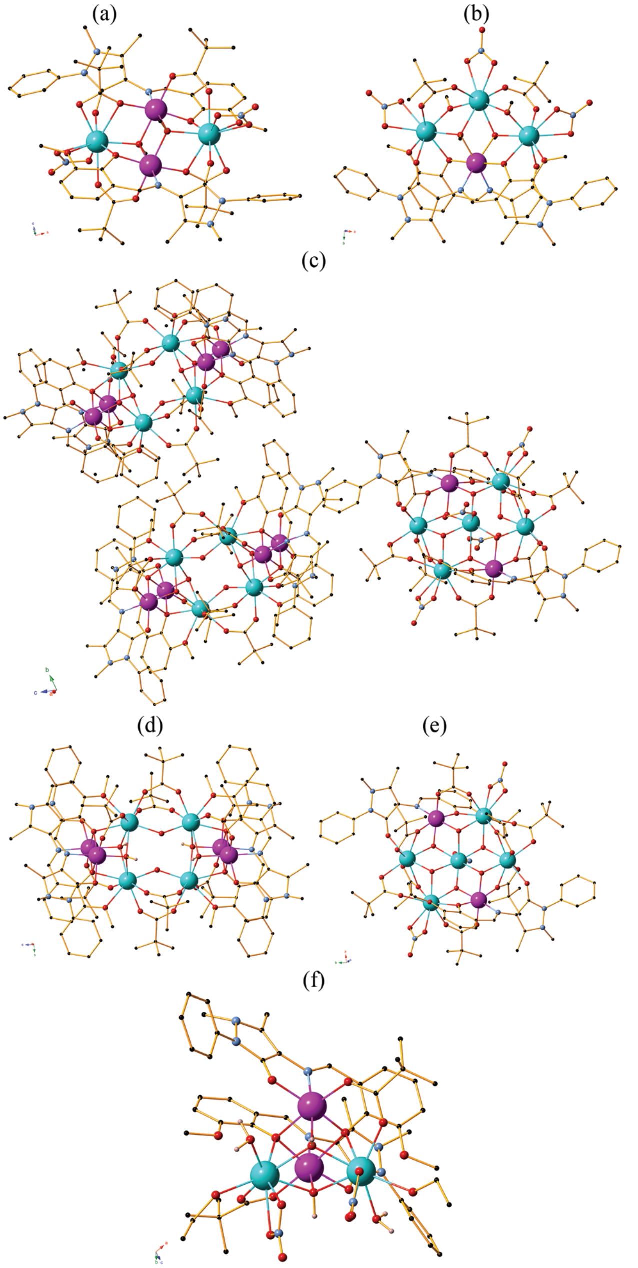


Fig. 1 Molecular structures of **3** (a), **4** (b), **5** (c), **6** (d), **7** (e) and **8** (f). Colour code: Co^{II}, pink; Dy^{III}, light blue; O, red; N, blue; C, black. Hydrogen atoms are omitted for clarity.

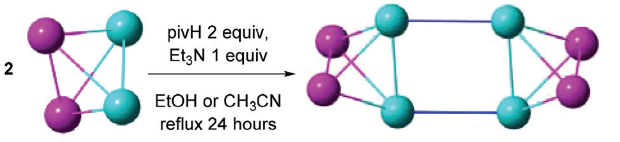
reaction in CH_3CN under reflux conditions for an hour (Table 1, entry 5), only compound **6**·$2CH_3CN$ was isolated and characterized (Fig. 1d). Compound **6** is identical to the octanuclear species found in **5**. The coordination number of the four Dy^{III} ions is 8. Using Shape software,[35] the geometry of both Dy^{III} ions can be best described as triangular dodecahedron, $S(P) = 0.790$.

A further increase of the reaction time to 24 hours (Table 1, entry 6) results in the isolation of only compound **7**·$4CH_3CN$ (Fig. 1e) which is identical to the heptanuclear species found in **5**. This indicates a rearrangement to a species in which the Co/Dy ratio is different. The coordination numbers of the three peripheral and the central Dy^{III} ions are 8 and 7, respectively. The geometry of the central Dy^{III} ion can be best described as capped octahedron and of the four wheel Dy^{III} as bicapped trigonal prism. Thus, the solvent has a major effect on the adopted topology in this family of CCs. The use of CH_3CN does not provide a link between the metal centres; instead it promotes hydrolysis of the metal salts to give CCs of higher nuclearity. The differences in temperature and reaction time in the synthesis of **5–7** influence the final product. A unit cell check of twenty random samples selected from three different vials gave identical unit cells, indicating that formation of **5–7** was reproducible.

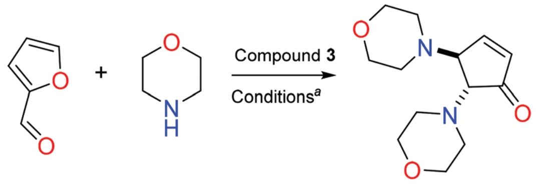
The next step was to incorporate a protic solvent that has similar coordination ability to MeOH but is more bulky. The additional bulk should prevent the formation of bridges to give the defect dicubane geometry. Indeed, a reaction in EtOH at 40 °C for 1 hour (Table 1, entry 7) resulted in the formation of a dicationic tetranuclear compound **8**·EtOH possessing a cubane (Fig. 1f) or **3M4-1** topology (Table 1, entry 7). Two triply bridging hydroxyl groups further enhance the formation of the cubane topology, while ethanol and water molecules fill the vacant positions on the two Dy^{III} centres. The coordination number of the two Dy^{III} ions is 9. The geometry of both Dy^{III} ions can be best described as Spherical capped square antiprism [$S(P) = 1.144$]. This cubane topology has been reported previously only once in Co/Ln chemistry.[53] Most of the known tetranuclear Co_2Dy_2 compounds possess a defect dicubane topology.

Thus, the employment of EtOH as a solvent prevents the formation of EtO bridges and promotes partial hydrolysis of the metal centres to give a cubane unit. From the decorated topologies[12] (Table 1, entries 7 or 8 and 5) compound **8** can be considered as half the octanuclear species found in **6**. **6** could be formed by linking two cubane units by double deprotonation of a coordinated H_2O molecule to form a μ_2-O bridge. At the same time, replacement of two coordinated NO_3, two EtOH and the remaining coordinated H_2O molecules in each cubane by pivalate groups further stabilizes the octanuclear species. The formation of **8** was achieved in one hour at 40 °C, thus the next step is to confirm that **8** is indeed an intermediate in the formation of **6**. This could be done in two ways: (a) by showing that an increase in temperature or time affords an octanuclear species isoskeletal to **6** and (b) by converting **8** to **6** in an independent reaction. Reaction under reflux conditions for an hour (Table 1, entry 8) afforded compound **8**·2(EtOH), which crystallized in a different space group. However, reaction for 24 hours under reflux (Table 1, entry 9) afforded compound **9**, isoskeletal to **6**. Furthermore, heating **8** for 24 hours under reflux in EtOH or CH_3CN, in the presence of 2 equivalents of pivalic acid and 1 equivalent of Et_3N, resulted in the formation of **9** or **6**, respectively (Scheme 3), as confirmed by unit cell check and IR.

To confirm the identity of these compounds in solution, we made use of electrospray ionization mass spectrometry



Scheme 3 A proposed transformation of **8** or **8′** to **9** (EtOH) or **6** (CH$_3$CN).



Scheme 4 The catalytic reaction tested for compound **3**.

Table 2 Comparison of catalytic activity for compound **3**

Entries	Catalyst loading^b (%)	2 h (yield %)^c	8 h (yield %)^c
1	10	92	95
2	5	86	90
3	2.5	73	85
4	1	43	66

^{a} Reaction conditions: morpholine 1 mmol; 2-furaldehyde 0.5 mmol; 4 Å MS 100 mg; catalyst; anhydrous MeCN 4 mL; room temperature. ^{b} Catalyst loading calculated per equivalent of Dy. ^{c} Determined by ^{1}H NMR spectroscopy.

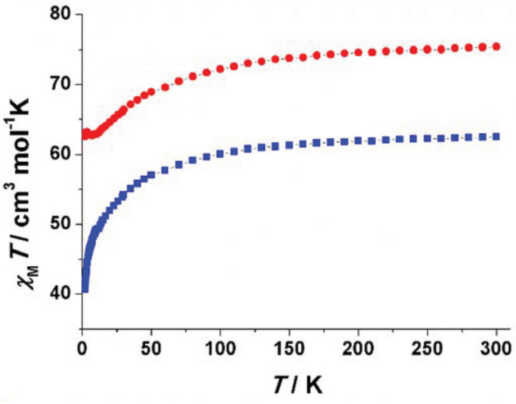


Fig. 2 $\chi_M T$ *vs.* T plots for complexes **6** (blue) and **7** (red). Solid lines are guides for the eye.

(ESI-MS). However only for compounds **3** and **8** were we able to ascertain the identities of the species in solution. For **3**, we observed two peaks in the MS (positive-ion mode) at *m*/*z* 1644.6395 and at *m*/*z* 791.3097 which correspond to the fragments, $[Co^{II}_2Dy^{III}_2(MeO)_2(C_{19}H_{18}N_3O_3)_2(C_5H_9O_2)_4(NO_3)]^+$ and $[Co^{II}_2Dy^{III}_2(MeO)_2(C_{19}H_{18}N_3O_3)_2(C_5H_9O_2)_4 - H]^{2+}$, respectively (see Fig. S7†). For **8**, we observed two peaks in the MS (positive-ion mode) at *m*/*z* 1709.3351 and at *m*/*z* 1644.2554 which correspond to two monocationic fragments, $[Co^{II}_2Dy^{III}_2(OH)_2(L)_2(piv)_2(NO_3)_4(EtOH)_2(H_2O) + H]^+$ and $[Co^{II}_2Dy^{III}_2(OH)_2(L)_2(piv)_2(NO_3)_4(EtOH)]^+$, respectively (see Fig. S8†). Assignments were confirmed by the Dy isotope patterns (the weaker patterns from Co were masked) and showed that the clusters identified in the solid state were preserved in solution.

Since a tetranuclear $Co^{II}_2Dy^{III}_2$ compound[9] is an efficient catalyst for the synthesis of *trans*-4,5-diaminocyclopent-2-enones from 2-furaldehyde and primary and secondary amines, we used compound **3** as a catalyst in this domino reaction (Scheme 4 and Table 2). Loadings of 1% and 2.5% for 2 h resulted in 43% and 73% yields, respectively. A loading of 10% for 8 h showed the highest yield of 95%. No significant improvement in yield was observed for any % loading over 8 hours. A fourfold decrease in catalyst loading for 8 h (2.5%) still shows good yields (85%), however these are lower than the previously mentioned $Co^{II}_2Dy^{III}_2$ compound,[9] suggesting that catalytic efficiency is highly dependent on the coordination environment of the Dy^{III} centres. Efforts to recover the catalyst were not successful, while theoretical studies on this aspect are in progress.

The room temperature $\chi_M T$ values for **6** and **7** (62.5 and 75.4 cm^3 K mol^{-1}, respectively) are in agreement with the expected values of 64.18 and 74.60 cm^3 K mol^{-1} for four non-interacting Dy^{III} ($^6H_{15/2}$ free ion; $S = 5/2$; $L = 5$; $g_J = 4/3$) centres, and four Co^{II} ions or five non-interacting Dy^{III} and two Co^{II} respectively (Fig. 2). Upon cooling, the $\chi_M T$ products decrease monotonically for **6** reaching 40.7 cm^3 K mol^{-1} at 2 K and down to a quasi-constant value around 63 cm^3 K mol^{-1} for **7**. This decrease is mainly due to the progressive depopulation of the Dy^{III} excited Stark sublevels. The relativity high $\chi_M T$ value and the absence of decay at low temperature for **7**, as well its fast magnetization (Fig. S10†), may also suggest weak intramolecular ferromagnetic coupling. In the light of the susceptibility responses, alternating-current (ac) preliminary magnetic susceptibility measurements were performed on polycrystalline samples of **6** and **7** (Fig. S11†). In a zero applied dc field and a 4 G ac field oscillating at 1000 and 10 Hz frequency-dependent out-of-phase (χ''_M) weak tails were observed, but no peaks were seen even under a dc field of 0.1 T, suggesting a weak single-molecule magnet response clearly below 2K.

The CCs presented here show how major differences in the core motif are caused by subtle changes in reaction conditions. The employment of HL in Co/Dy chemistry affords, compounds (a) with Co in oxidation state II and (b) with hitherto unobserved topologies that are preserved in alcoholic solvents. The most important feature of HL is that despite being monoanionic and showing a coordination environment similar to that in other ligands,[18] it gives CCs with higher nuclearity. Two different coordination modes are seen for HL in compounds **3–9** (Scheme 2), however despite the increase in reaction temperature no increase in the number of bridging metal centres is observed. In protic solvents, the ligand coordinates differently, but this can be attributed to the existence of further MeO bridges. The final products are influenced by the temperature and the reaction time. When CH_3CN is used as a solvent, a mixed octanuclear and heptanuclear CC product is obtained (Table 1, entry 4) and when the reaction takes place under reflux (Table 1, entries 5 and 6), distinct octanuclear (Table 1, entry 5) and heptanuclear (Table 1, entry 6) CCs are obtained. Even with changes of solvents *viz.* to CH_3CN (Table 1, entry 5) and EtOH (Table 1, entry 9) and reaction times, isoskeletal products are obtained. For this specific reaction system, an increase in the reaction temperature enhances deprotonation of water molecules to form OH^- and/or O^{2-} species leading to CC clusters of higher nuclearity in CH_3CN and EtOH.

Conclusions

The formation of the double cubane **9** either from the single cubane **8** or by increased reaction time and temperature (Table 1, entry 9) represents an interesting example in coordination chemistry. The structural relationship of compounds **6**, **9** and **8** can immediately be visualized (Scheme 3) from topological analysis. Since the coordination chemistry of HL is still insufficiently delineated, further studies are required that will reveal its coordination behaviour and lead to a library of CCs. We are extending this study to: (a) more complicated systems to explore synthesis of CCs with higher nuclearity and (b) compounds of other 3d and 4f elements to investigate their magnetic and photoluminescent properties.

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References

1 D. I. Alexandropoulos, T. N. Nguyen, L. Cunha-Silva, T. F. Zafiropoulos, A. Escuer, G. Christou and T. C. Stamatatos, *Inorg. Chem.*, 2013, **52**, 1179–1181.

2 J.-B. Peng, Q.-C. Zhang, X.-J. Kong, Y.-Z. Zheng, Y.-P. Ren, L.-S. Long, R.-B. Huang, L.-S. Zheng and Z. Zheng, *J. Am. Chem. Soc.*, 2012, **134**, 3314–3317.

3 C. Papatriantafyllopoulou, T. C. Stamatatos, C. G. Efthymiou, L. Cunha-Silva, F. A. A. Paz, S. P. Perlepes and G. Christou, *Inorg. Chem.*, 2010, **49**, 9743–9745.

4 Y.-Z. Zheng, M. Evangelisti and R. E. P. Winpenny, *Chem. Sci.*, 2011, **2**, 99–102.

5 S. Hossain, S. Das, A. Chakraborty, F. Lloret, J. Cano, E. Pardo and V. Chandrasekhar, *Dalton Trans.*, 2014, **43**, 10164–10174.

6 G. Maayan and G. Christou, *Inorg. Chem.*, 2011, **50**, 7015–7021.

7 K. Liu, W. Shi and P. Cheng, *Coord. Chem. Rev.*, 2015, **289–290**, 74–122.

8 E. C. Sañudo and L. Rosado Piquer, *Dalton Trans.*, 2015, **44**, 8771–8780.

9 K. Griffiths, C. W. D. Gallop, A. Abdul-Sada, A. Vargas, O. Navarro and G. E. Kostakis, *Chem. – Eur. J.*, 2015, **21**, 6358–6361.

10 R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 2002, 1–10.

11 M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782–1789.

12 G. E. Kostakis and A. K. Powell, *Coord. Chem. Rev.*, 2009, **253**, 2686–2697.

13 G. E. Kostakis, V. A. Blatov and D. M. Proserpio, *Dalton Trans.*, 2012, **41**, 4634–4640.

14 G. E. Kostakis, S. P. Perlepes, V. A. Blatov, D. M. Proserpio and A. K. Powell, *Coord. Chem. Rev.*, 2012, **256**, 1246–1278.

15 P. Wix, G. E. Kostakis, V. A. Blatov, D. M. Proserpio, S. P. Perlepes and A. K. Powell, *Eur. J. Inorg. Chem.*, 2013, **2013**, 520–526.

16 G. E. Kostakis and A. K. Powell, *Chem. – Eur. J.*, 2010, **16**, 7983–7987.

17 E. Loukopoulos, B. Berkoff, A. Abdul-Sada, G. J. Tizzard, S. J. Coles, A. Escuer and G. E. Kostakis, *Eur. J. Inorg. Chem.*, 2015, 2646–2649.

18 K. C. Mondal, A. Sundt, Y. Lan, G. E. Kostakis, O. Waldmann, L. Ungur, L. F. Chibotaru, C. E. Anson and A. K. Powell, *Angew. Chem., Int. Ed.*, 2012, **51**, 7550–7554.

19 E. V. Orlova, A. E. Goldberg, M. A. Kiskin, P. S. Koroteev, A. L. Emelina, M. A. Bykov, G. G. Aleksandrov, Z. V. Dobrokhotova, V. M. Novotortsev and I. L. Eremenko, *Russ. Chem. Bull.*, 2012, **60**, 2236–2250.

20 N. P. Burkovskaya, E. V. Orlova, M. A. Kiskin, N. N. Efimov, A. S. Bogomyakov, M. V. Fedin, S. V. Kolotilov, V. V. Minin, G. G. Aleksandrov, A. A. Sidorov, V. I. Ovcharenko, V. M. Novotortsev and I. L. Eremenko, *Russ. Chem. Bull.*, 2012, **60**, 2490–2503.

21 N. Gogoleva, E. Zorina-Tikhonova, G. Aleksandrov, A. Lermontov, N. Efimov, A. Bogomyakov, E. Ugolkova, S. Kolotilov, A. Sidorov, V. Minin, V. Novotortsev and I. Eremenko, *J. Cluster Sci.*, 2014, **26**, 137–155.

22 E. N. Egorov, E. A. Mikhalyova, M. A. Kiskin, V. V. Pavlishchuk, A. A. Sidorov and I. L. Eremenko, *Russ. Chem. Bull.*, 2014, **62**, 2141–2149.

23 S. Schmidt, D. Prodius, G. Novitchi, V. Mereacre, G. E. Kostakis and A. K. Powell, *Chem. Commun.*, 2012, **48**, 9825–9827.

24 V. Mereacre, A. M. Ako, R. Clérac, W. Wernsdorfer, I. J. Hewitt, C. E. Anson and A. K. Powell, *Chem. – Eur. J.*, 2008, **14**, 3577–3584.

25 G. Peng, G. E. Kostakis, Y. Lan and A. K. Powell, *Dalton Trans.*, 2013, **42**, 46–49.

26 S. J. Coles and P. A. Gale, *Chem. Sci.*, 2012, **3**, 683–689.

27 O. V. Dolomanov, A. J. Blake, N. R. Champness and M. Schröder, *J. Appl. Crystallogr.*, 2003, **36**, 1283–1284.

28 L. Palatinus and G. Chapuis, *J. Appl. Crystallogr.*, 2007, **40**, 786–790.

29 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.

30 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2015, **71**, 3–8.

31 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112–122.

32 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.

33 C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. Van De Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453–457.

34 P. King, R. Clerac, W. Wernsdorfer, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2004, 2670–2676.

35 S. A. M. Llunell, D. Casanova, J. Cirera and P. Alemany, *SHAPE version 2.0*, 2010, Barcelona.

36 N. W. Johnson, *Can. J. Math.*, 1966, **18**, 169–200.

37 A. K. Powell, S. L. Heath, D. Gatteschi, L. Pardi, R. Sessoli, G. Spina, F. Del Giallo and F. Pieralli, *J. Am. Chem. Soc.*, 1995, **117**, 2491–2502.

38 L. C. Roof, W. T. Pennington and J. W. Kolis, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 913–915.

39 L. Cai, B. M. Segal, J. R. Long, M. J. Scott and R. H. Holm, *J. Am. Chem. Soc.*, 1995, **117**, 8863–8864.

40 A. F. Armstrong, T. Chivers, M. Krahn and M. Parvez, *Can. J. Chem.*, 2005, **83**, 1768–1778.

41 A. S. R. Chesman, D. R. Turner, B. Moubaraki, K. S. Murray, G. B. Deacon and S. R. Batten, *Dalton Trans.*, 2012, **41**, 3751–3757.

42 A. A. Kitos, C. G. Efthymiou, C. Papatriantafyllopoulou, V. Nastopoulos, A. J. Tasiopoulos, M. J. Manos, W. Wernsdorfer, G. Christou and S. P. Perlepes, *Polyhedron*, 2011, **30**, 2987–2996.

43 R. Pattacini, P. Teo, J. Zhang, Y. Lan, A. K. Powell, J. Nehrkorn, O. Waldmann, T. S. A. Hor and P. Braunstein, *Dalton Trans.*, 2011, **40**, 10526–10534.

44 L. F. Chibotaru, L. Ungur, C. Aronica, H. Elmoll, G. Pilet and D. Luneau, *J. Am. Chem. Soc.*, 2008, **130**, 12445–12455.

45 J. W. Sharples, Y.-Z. Zheng, F. Tuna, E. J. L. McInnes and D. Collison, *Chem. Commun.*, 2011, **47**, 7650–7652.

46 J. Liu, C. Ma, H. Chen, M. Hu, H. Wen, H. Cui and C. Chen, *Dalton Trans.*, 2013, **42**, 3787–3790.

47 V. Chandrasekhar, A. Dey, S. Das, M. Rouxieres and R. Clerac, *Inorg. Chem.*, 2013, **52**, 2588–2598.

48 A. J. Tasiopoulos, P. L. Milligan, K. A. Abboud, T. A. O'Brien and G. Christou, *Inorg. Chem.*, 2007, **46**, 9678–9691.

49 A. J. Tasiopoulos, T. A. O'Brien, K. A. Abboud and G. Christou, *Angew. Chem. Int. Ed.*, 2004, **43**, 345.

50 Y.-J. Zhang, B.-Q. Ma, S. Gao, J.-R. Li, Q.-D. Liu, G.-H. Wen and X.-X. Zhang, *J. Chem. Soc. Dalton Trans.*, 2000, 2249.

51 A. J. Wooles, O. J. Cooper, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Organometallics*, 2010, **29**, 2315–2321.

52 M. P. Coles, P. B. Hitchcock, A. V. Khvostov, M. F. Lappert, Z. Li and A. V. Protchenko, *Dalton Trans.*, 2010, **39**, 6780–6788.

53 X.-Q. Zhao, Y. Lan, B. Zhao, P. Cheng, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2010, **39**, 4911–4917.