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First example of 3d/Dy^{III} coordination clusters as catalysts in a domino reaction

Kieran Griffiths,^[a] Christopher W. D. Gallop,^[a] Alaa Abdul-Sada,^[a] Alfredo Vargas,^[a] Oscar Navarro^[a] and George E. Kostakis^{*[a]}

In memory of Prof. Yiannis Elemen

Abstract: Three isoskeletal tetranuclear coordination clusters with general formula $[M^II_2Dy^{III}_2L_4(EtOH)_6](ClO_4)_2 \cdot 2(EtOH)$, ($M = Co$, **1**; $M = Ni$, **2**) and $[Ni^{II}_2Dy^{III}_2L_4Cl_2(CH_3CN)_2] \cdot 2(CH_3CN)$ (**3**), have been synthesized and characterized. These air-stable compounds, and in particular **3**, display efficient homogeneous catalytic behavior towards the room temperature synthesis of *trans*-4,5-diaminocyclopent-2-enones from 2-furaldehyde and primary or secondary amines under a non-inert atmosphere.

In the last two decades interest in the construction of polynuclear 3d/4f Coordination Clusters (CCs)^[1] was driven by their aesthetically pleasing structures,^[2–4] however the interest burgeoned due to the inartistic magnetic properties that such species display.^[5–7] The synthesis of such species can be aptly described by the term “Serendipitous Self Assembly”^[8] but, in recent years, tremendous attention has been given on the selection of the appropriate organic ligands to develop the syntheses of such CCs. Apart from the employment of an heptanuclear Ce^{IV}Mn^{IV}₆ CC for the oxidation of benzyl alcohol to benzaldehyde, less attention has been given to the catalytic properties of such heteronuclear compounds.^[9] For instance, dysprosium triflate, due to its mild nature, has proven to be an excellent catalyst for reactions where both nitrogen and oxygen functionalities are present.^[10] Of particular interest is its ability to retain catalytic activity in the presence of Lewis-basic nitrogen groups, allowing for its use in transformations involving unprotected amines.^[11–16]

We recently initiated a project aiming to develop dual catalytic CCs and to achieve this goal, compounds that retain their topology into the solution are required. 3d/Dy^{III} CCs possessing a defect dicubane topology derived from (*E*)-2-(2-hydroxy-3-methoxybenzylidene-amino)phenol (*H*₂L),^[17] pose as ideal candidates to serve this purpose. *H*₂L supports a defect dicubane topology bearing two divalent 3d ions and two trivalent 4f ions^[18,19] in the absence of any additional bridging atom. Indeed, the combination in open air of *H*₂L with Dy(OTf)₃ and Co(ClO₄)₂·6H₂O or Ni(ClO₄)₂·6H₂O in the presence of Et₃N in EtOH afforded air-stable tetranuclear defect dicubane compounds with general formula $[M^II_2Dy^{III}_2L_4(EtOH)_6](ClO_4)_2 \cdot 2(EtOH)$ ($M = Co$, **1**; $M = Ni$, **2**) (Figure 1). Each 3d center has an octahedral geometry and each Dy^{III} center has

square antiprismatic geometry. Two different coordination modes can be found for the organic ligand (Scheme S1), occupying five and six vertices for the 3d and the Dy^{III} centers, respectively. The remaining vertices are occupied by one (3d) and two (Dy^{III}) ethanol molecules. To further confirm the identity of compounds **1** and **2** in solution, we performed a broad electrospray ionization mass (ESI-MS) spectrometry study. For **1**, we observed two peaks in the MS (positive ion mode) at 1506.9719 m/z and at 736.0393 m/z which perfectly correspond to two fragments, $[Co^{II}_2Dy^{III}_2L_4(ClO_4)-H]^+$ and $[Co^{II}_2Dy^{III}_2L_4(MeOH)_2-H]^{2+}$, respectively (Figs S1–S2). Similarly, for **2**, peaks at 1520.0169 and 744.55 correspond to $[Ni^{II}_2Dy^{III}_2L_4(MeOH)_2(EtOH)]+2H]^+$ and $[Ni^{II}_2Dy^{III}_2L_4(MeOH)-(EtOH)]+2H]^{2+}$ fragments (Figs S3–S4), respectively. Therefore, in both cases, the ESI-MS data indicate that the dicationic $[M^II_2Dy^{III}_2L_4]^{2+}$ cores remain intact.

Figure 1. Molecular structure of **2** (**1** is isostructural with Co^{II} atoms in the Ni^{II} positions). Colour code: Ni^{II}, green; Dy^{III}, light blue; O, red; N, blue; C, black; Cl, purple. Hydrogen atoms are omitted for clarity

With the CCs in hand, the next step was to identify a challenging catalytic reaction. Batey and co-workers reported on the use of Dy(OTf)₃ as a Lewis acid catalyst for the domino condensation/ring-opening/electrocyclization of secondary amines and 2-furaldehyde,^[14] leading to the synthesis of exclusively *trans*-4,5-diaminocyclopent-2-enones. This is a remarkably atom-efficient reaction with only 1 equivalent of water generated as a sub-product. The authors postulated that the reaction proceeds through a deprotonated Stenhouse salt intermediate,^[20] although they showed that the lanthanide is not involved in the cyclization step (Scheme 1). Primary amines required the use of more expensive Sc(OTf)₃ to produce the corresponding products, albeit in considerably lower yields.

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Supporting information for this article is given via a link at the end of the document.

Scheme 1. Proposed mechanism for the Dy^{III}-catalyzed synthesis of *trans*-4,5-diaminocyclopent-2-enones

In this protocol, the reactions were performed in acetonitrile under a nitrogen atmosphere, at room temperature and using a catalyst loading of 10 mol%.^[14] Under these conditions, the reaction between 2-furaldehyde and morpholine led to a quantitative amount of (4*S*,5*R*)-dimorpholinocyclopent-2-enone (Table 1, entry 1). This reaction was chosen to test the catalytic activity of CCs **1** and **2**. To make the protocol more user-friendly, all reactions were carried out in open air. Both complexes afforded moderate yields of the desired product after 16 h (Table 1, entries 2 and 3). Upon increasing the temperature (reflux), both complexes allowed for the reaction to take place in excellent yields, in almost one order of magnitude less time (2 h) (Table 1, entries 4 and 5). At this temperature and in both cases, the catalyst loading could be decreased to 2.5 mol% with only a slight decrease in the yields (Table 1, entries 6–11). Interestingly, the use of Dy(OTf)₃ under these conditions led to a considerable decrease in the yield when compared with the reaction at room temperature (Table 1, entry 12). As expected, neither Co(ClO₄)₂·6(H₂O) nor Ni(ClO₄)₂·6(H₂O), the 3d metal precursors used in the synthesis of the CCs, showed catalytic behaviour (Table 1, entries 13–14).

Figure 2. Molecular structure of **3**. Colour code: Ni^{II}, green; Dy^{III}, light blue; O, red; N, blue; C, black.; Cl, purple. Hydrogen atoms are omitted for clarity.

The excellent results at high temperature, using low catalyst loadings, prompted us to consider the possibility that **1**

and **2** were undergoing changes under our reaction conditions. To investigate this hypothesis, the best performing CC, **2**, was refluxed in acetonitrile for 1 h, affording an air-stable, compound formulated as [Ni^{II}₂Dy^{III}₂L₄Cl₂(CH₃CN)₂·2(CH₃CN) (**3**) (Figure 2).^[21] A similar coordination behavior to **1** and **2** (Scheme S1) is observed for the organic moieties in **3** but, interestingly, a perchlorate to chlorine transformation is observed.^[22] The Ni^{II} atoms have an octahedral geometry with one vertex occupied by a CH₃CN molecule, while Dy^{III} has almost ideal pentagonal bipyramidal geometry; one phenolic oxygen and the chlorine atoms occupy the axial positions. ESI-MS studies showed that **3** retains its topology in solution. Only two fragments are observed and the two main peaks at 1556.1150 and 703.5109 correspond to [(Ni^{II}₂Dy^{III}₂L₄Cl₂(CH₃CN)(CH₃OH)]⁺+4H⁺ and [(Ni^{II}₂Dy^{III}₂L₄)]²⁺ fragments (Figs S5–S6), respectively.

Table 1. Comparison of catalytic activity for compounds **1**, **2** and **3**.^[a]

Entries	Catalyst	T	Loading (mol%) ^[b]	Time (h)	Yield (%)
1	Dy(OTf) ₃	r.t.	10	16	Quantitative ^[14]
2	1	r.t.	10	16	55
3	2	r.t.	10	16	41
4	1	reflux	10	2	93
5	2	reflux	10	2	95
6	1	reflux	5	2	92 ^[c]
7	1	reflux	2.5	2	90 ^[c]
8	1	reflux	1	2	79 ^[c]
9	2	reflux	5	2	94 ^[c]
10	2	reflux	2.5	2	94 ^[c]
11	2	reflux	1	2	80 ^[c]
12	Dy(OTf) ₃	reflux	10	2	63
13	Co(ClO ₄) ₂ ·6(H ₂ O)	reflux	10	2	0
14	Ni(ClO ₄) ₂ ·6(H ₂ O)	reflux	10	2	0
15	3	r.t.	1	16	Quantitative

[a] Reaction conditions: amine, 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 ¹H NMR spectroscopy.

The use of only 1 mol% of **3** at room temperature in our test catalytic reaction led to the quantitative formation of the desired product (Table 1, entry 15). This is a decrease of catalyst loading of one order of magnitude when compared to the state-of-the-art for this multicomponent reaction, as well as a more user-friendly protocol that does not require the use of an inert atmosphere. Realizing the convenience of circumventing the need to synthesize **2** to obtain **3**, we modified the original procedure for the synthesis of **2** by substituting ethanol by acetonitrile and refluxing for 1 h, affording **3** in 68% yield.

We then explored the scope of the reaction by employing a variety of secondary amines as substrates (Table 2). In all cases, the reactions proceeded smoothly and it was possible to isolate the corresponding products **4a–4e** in excellent yields. To our

delight, when the same conditions were applied to primary amines, **3** catalyzed the formation of the corresponding deprotonated Stenhouse salts (**5a-d**). The combination of **5a** or **5b** with very dilute HCl or silica gel promoted the ring-closing leading to the corresponding *trans*-4,5-diaminocyclopent-2-enones in very high yields (95% and 56% overall yield, for **4f** and **4g**, respectively, see Scheme S2). The latter transformations are consistent with Batey's proposition that Dy^{III} is not involved in the cyclization step. Interestingly, the same treatment applied to **5c** and **5d** did not afford the cyclized products to any extent, the substrates remaining unaltered.

Table 2. Dy^{III} catalysed condensation/ring-opening/cyclization of secondary amines with 2-furaldehyde and condensation/ring-opening of primary amines with 2-furaldehyde.

[a] Reaction conditions: amine, 1 mmol; 2-furaldehyde, 0.5 mmol; 4 Å MS, 100 mg; catalyst; anhydrous MeCN, 4 mL; room temperature.

To further identify the formation of the deprotonated Stenhouse salt intermediate a computational study was undertaken. Energy minimization calculations within the Kohn-Sham Density Functional (DFT) at the B3LYP/6-311G** level employing the polarizable continuum media (PCM) formalism were undertaken of model compounds **4f**, **5a**, **6**, and **7** (Figure 3). The overall energy profile together with the calculated NMR data (Table T1) highly suggests that a) the pathway from intermediate **6-5a** towards the final product is highly favorable – which thus confirms that the catalysis takes place prior to this step, b) intermediate **6-5a** likely resembles a configuration somewhere between **6** (in which the nitrogen bears a hydrogen) and **5a** (in which the hydrogen the migrates to the neighboring oxygen) c) one factor that highly affects the total electronic energy of **7** concerns a pyramidal-to-planar evolution of the beta-nitrogen, a key feature that is likely involved in the catalytic process.

Figure 3. Energy profile of the reaction with aniline of the ring opening (**5a**) and closure (**4f**) products.

In conclusion, we report herein the first examples of a series of custom-designed, catalytically active 3d/Dy^{III} CCs. These are the first results towards the development of dual catalytic CCs. A careful choice of the organic ligand has allowed for the synthesis of CCs that remain intact into solution and display a remarkable catalytic activity. The catalytic performance can be improved by modifying the coordination environment of the Dy^{III} ion. This control allows, for the first time, a thorough catalytic investigation of this species. NMR of the diamagnetic (Ni^{II}Y^{III})₂ analogue as well theoretical studies of the active catalytic species are underway. As the synthetic strategy of **1-3** is simple, high yielding and based on accessible building blocks, the approach is likely widely applicable and new reactivity, including the 3d part, can be uncovered.

Experimental Section

Synthesis: **1** and **2**. Dy(OTf)₃ (61 mg, 0.1 mmol), M(ClO₄)₂·6H₂O (37 mg for **1** or 37 mg for **2**, 0.1 mmol), LH₂ (48 mg, 0.2 mmol) and Et₃N (69 µl, 0.5 mmol) were added in EtOH (20 mL), and the resulting mixture was stirred for 1 hour. After filtration, yellow-greenish (for **1**) and orange (for **2**) crystals were obtained in 49 % (for **1**) and 57 % (for **2**) yield and collected by filtration, washed with Et₂O and dried in air. **3**. Dy(OTf)₃ (61 mg, 0.1 mmol), Ni(ClO₄)₂·6H₂O (37 mg, 0.1 mmol), LH₂ (48 mg, 0.2 mmol) and Et₃N (69 µl, 0.5 mmol) were added in CH₃CN (20 mL), and the resulting mixture was refluxed for 1 hour. After filtration, yellow-greenish crystals were obtained in 68 % yield and collected by filtration, washed with Et₂O and dried in air. **Compound 3 can be synthesized at the same yield, altering Ni(ClO₄)₂·6H₂O with NiCl₂·6H₂O.**

Crystallography: C₇₂H₉₂Cl₂Co₂Dy₂N₄O₂₈ (**1**) (*M* = 1975.25 g/mol): monoclinic, space group P2₁/n (no. 14), *a* = 12.8246(4) Å, *b* = 20.9395(5) Å, *c* = 15.3815(5) Å, β = 108.997(4)°, *V* = 3905.6(2) Å³, *Z* = 2, *T* = 173.0 K, μ(CuKα) = 14.667 mm⁻¹, *D*_{calc} = 1.680 g/cm³, 25962 reflections measured (7.4° ≤ 2θ ≤ 142.898°), 7561 unique (*R*_{int} = 0.0490, *R*_{sigma} = 0.0482) which were used in all calculations. The final *R*₁ was 0.0378 (*I* > 2σ(*I*)) and *wR*₂ was 0.0981 (all data). C₇₂H₉₂Cl₂Dy₂N₄Ni₂O₂₈ (**2**) (*M* = 1974.81 g/mol): monoclinic, space group P2₁/n (no. 14), *a* = 12.7440(4) Å, *b* = 20.9329(5) Å, *c* = 15.3458(5) Å, β = 108.920(4)°, *V* = 3872.6(2) Å³, *Z* = 2, *T* = 173 K, μ(MoKα) = 2.539 mm⁻¹, *D*_{calc} = 1.694 g/cm³, 19340 reflections measured (4.798° ≤ 2θ ≤ 58.67°), 8980 unique (*R*_{int} = 0.0330, *R*_{sigma} = 0.0510) which were used in all calculations. The final *R*₁ was 0.0374 (*I* > 2σ(*I*)) and *wR*₂ was 0.0883 (all data). C₆₄H₅₆Cl₂Dy₂N₄Ni₂O₁₂ (**3**) (*M* = 1642.48 g/mol): triclinic, space group P-1 (no. 2), *a* = 11.696(3) Å, *b* = 11.973(4) Å, *c* = 13.084(4) Å, α = 88.597(16)°, β = 64.494(10)°, γ = 81.504(15)°, *V* = 1633.9(9) Å³, *Z* = 1, *T* = 100 K, μ(MoKα) = 2.975 mm⁻¹, *D*_{calc} = 1.669 g/cm³, 17540 reflections measured (4.768° ≤ 2θ ≤ 50.166°), 5747 unique (*R*_{int} = 0.1336, *R*_{sigma} = 0.1333) which were used in all calculations. The final *R*₁ was 0.0655 (*I* > 2σ(*I*)) and *wR*₂ was 0.1584 (all data). CCDC 1012311-1012312-1038641. Electronic Supplementary Information (ESI) available: [Figs S1- S6, Table T1, Schemes S1-S2, NMR, IR, HRMS data, Computational details].

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Keywords: coordination cluster • catalysis • dysprosium • domino reactions • amines

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Acknowledgements

Entry for the Table of Contents
COMMUNICATION

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