Heteronuclear 3 d/DyIII coordination clusters as catalysts in a domino reaction

Article  (Accepted Version)


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In the last two decades interest in the construction of polynuclear 3d/4f Coordination Clusters (CCs) was driven by their aesthetically pleasing structures, however the interest burgeoned due to the intrinsic magnetic properties that such species display. The synthesis of such species can be aptly described by the term “Serendipitous Self Assembly” 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⁻⁷Mn⁻⁶ CC for the oxidation of benzyl alcohol to benzaldehyde, less attention has been given to the catalytic properties of such heteronuclear compounds. 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. 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.

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/Dy³ CCs possessing a defect dicubane topology derived from (E)-2-(2-hydroxy-3-methoxybenzylidene-amino)phenol (MeOH) [17] pose as ideal candidates to serve this purpose. H₂L 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 H₂L with Dy(OIT)₃ and Co(CIO₄)₂·6H₂O or Ni(CIO₄)₂·6H₂O in the presence of Et₃N in EtOH afforded air-stable tetranuclear defect dicubane compounds with general formula [MIII⁺²⁴DyIII⁺₈L₄(EtOH)₄] · (CIO₄)₂ · 2(EtOH) (M = Co; 1; M = Ni; 2) (Figure 1). Each 3d center has an octahedral geometry and each Dy³ 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 Dy³ centers, respectively. The remaining vertices are occupied by one (3d) and two (Dy³) 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 736.0393 m/z which perfectly correspond to two fragments, [CoII⁺²⁴DyIII⁺₈L₄(CIO₄)₂]⁺ and [CoII⁺²⁴DyIII⁺₈L₄(MeOH)₂·H]⁺, respectively (Figs S1-S2). Similarly, for 2, peaks at 1520.0169 and 744.55 correspond to {[NiII⁺²⁴DyIII⁺₈L₄(MeOH)₂(EtOH)]+·2H}⁺ and {[NiII⁺²⁴DyIII⁺₈L₄(MeOH)·(EtOH)]⁺·2H}⁺ fragments (Figs S3-S4), respectively. Therefore, in both cases, the ESI-MS data indicate that the dicarboxylic [M⁺²⁴Dy III⁺₈L₂]⁺ cores remain intact.

With the CCs in hand, the next step was to identify a challenging catalytic reaction. Bayley and co-workers reported on the use of Dy(OIT)₃ as a Lewis acid catalyst for the domino condensation/ring-opening/electrocyclization of secondary amines and 2-furaldehyde, 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 Stienhouse salt intermediate, although they showed that the lanthanide is not involved in the cyclization step (Scheme 1). Primary amines required the use of more expensive Sc(OIT)₃ to produce the corresponding products, albeit in considerably lower yields.
In this protocol, the reactions were performed in acetonitrile under a nitrogen atmosphere, at room temperature and using a catalyst loading of 10 mol%. Under these conditions, the reaction between 2-furaldehyde and morpholine led to a quantitative amount of 1,4-diaminocyclopent-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 1-3). 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 behavior (Table 1, entries 13-14).

<table>
<thead>
<tr>
<th>Entries</th>
<th>Catalyst</th>
<th>T</th>
<th>Loading (mol%)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
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<tr>
<td>1</td>
<td>Dy(OTf)₃</td>
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<td>10</td>
<td>16</td>
<td>Quantitative¹⁴</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>r.t.</td>
<td>10</td>
<td>16</td>
<td>55</td>
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<tr>
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<td>2</td>
<td>r.t.</td>
<td>10</td>
<td>16</td>
<td>41</td>
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<tr>
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<td>2</td>
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</tr>
<tr>
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<td>reflux</td>
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<tr>
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<td>Co(ClO₄)₂·6(H₂O)</td>
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<td>2</td>
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<tr>
<td>14</td>
<td>Ni(ClO₄)₂·6(H₂O)</td>
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</tr>
<tr>
<td>15</td>
<td>3</td>
<td>r.t.</td>
<td>1</td>
<td>16</td>
<td>Quantitative</td>
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</table>

[¹] Reaction conditions: amine, 1 mmol; 2-furaldehyde, 0.5 mmol; 4 Å MS, 100 mg; 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

![Scheme 1. Proposed mechanism for the DyIII-catalyzed synthesis of trans-4,5-diaminocyclopent-2-enones](image)

![Figure 2. Molecular structure of 3. Colour code: Ni, green; DyIII, light blue; O, red; N, blue; C, black.; Cl, purple. Hydrogen atoms are omitted for clarity.](image)
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 DyIII 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. DyIII catalysed condensation/ring-opening/cyclization of secondary amines with 2-furaldehyde and condensation/ring-opening of primary amines with 2-furaldehyde.

| Reaction conditions: amine, 1 mmol; 2-furaldehyde, 0.5 mmol; 4 Å MS, 100 mg; catalyst; anhydrous MeCN, 4 mL; room temperature.  |
|---|---|---|
| 4a | n = 1, quantitative |  |
| 4b | n = 1, 99% |  |
| 4c | n = 1, 95% |  |
| 4d | n = 1, 61%  
  n = 2.5, 99% |  |
| 4e | n = 1, 63%  
  n = 2.5, 99% |  |
| 5a | n = 1, 96% |  |
| 5b | n = 1, 62% |  |
| 5c | n = 1, 78% |  |
| 5d | n = 1, 28%[8] |  |

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 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/DyIII 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 DyIII ion. This control allows, for the first time, a thorough catalytic investigation of this species. NMR of the diamagnetic (NiII2YIII2) analogue as well theoretical studies of the active catalytic specie 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.

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

Synthesis: 1 and 2. Dy(OI)$_2$ (61 mg, 0.1 mmol), M(ClO)$_4$ 6H$_2$O (37 mg for 1 or 37 mg for 2, 0.1 mmol), LH$_4$ (48 mg, 0.2 mmol) and Et$_2$N (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 Et$_2$O and dried in air. 3. Dy(OI)$_2$ (61 mg, 0.1 mmol), Ni(ClO)$_4$ 6H$_2$O (37 mg, 0.1 mmol), LH$_4$ (48 mg, 0.2 mmol) and Et$_2$N (69 µl, 0.5 mmol) were added in CH$_2$CN (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 Et$_2$O and dried in air. Compound 3 can be synthesized at the same yield, altering Ni(ClO)$_4$ 6H$_2$O with NiCl$_2$ 6H$_2$O.

Crystallography: C$_2$H$_6$Cl$_2$Co$_2$Dy$_2$NiO$_{18}$ (1) (M=1975.25 g/mol): monoclinic, space group P2/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) Å$^3$, Z = 2, T = 173.0 K, μ(CuKα) = 14.667 mm$^{-1}$, Dcalc = 1.680 g/cm$^3$, 25962 reflections measured (7.4° ≤ 2θ ≤ 142.88°), 7561 unique (R$_{int}$ = 0.0490, R$_{reps}$ = 0.0482) which were used in all calculations. The final R$_f$ was 0.0378 (I > 2σ(I)) and wR$_f$ was 0.0981 (all data). Cu$_2$H$_6$Cl$_2$Dy$_2$NiO$_{18}$ (2) (M=1794.81 g/mol): monoclinic, space group P2/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) Å$^3$, Z = 2, T = 173 K, μ(MoKα) = 2.539 mm$^{-1}$, Dcalc = 1.694 g/cm$^3$, 19340 reflections measured (4.798° ≤ 2θ ≤ 58.67°), 8980 unique (R$_f$ = 0.0330, R$_{reps}$ = 0.0510) which were used in all calculations. The final R$_f$ was 0.0374 (I > 2σ(I)) and wR$_f$ was 0.0883 (all data). Cu$_2$H$_6$Cl$_2$Dy$_2$NiO$_{18}$ (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(2) Å$^3$, Z = 1, T = 100 K, μ(MoKα) = 2.975 mm$^{-1}$, Dcalc = 1.669 g/cm$^3$, 17540 reflections measured (4.768° ≤ 2θ ≤ 50.166°), 5747 unique (R$_f$ = 0.1336, R$_{reps}$ = 0.1333) which were used in all calculations. The final R$_f$ was 0.0655 (I > 2σ(I)) and wR$_f$ was 0.1584 (all data). CCDC 1012311-10398641, Electronic Supplementary Information (ESI) available: [Figs S1- S6, Table T1, Schemes S1-S2, NMR IR, HRMS data, Computational details].

Acknowledgements

We thank the EPSRC UK National Crystallography Service at the University of Southampton for the collection of the crystallographic data for compound 3. G.E.K. acknowledges University of Sussex for offering a PhD position (K.G.).

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

Three air stable compounds formulated as 
\[ [\text{M}^{\text{II}}_2\text{Dy}^{\text{III}}_2\text{L}_4(\text{EtOH})_6](\text{ClO}_4)_2 2(\text{EtOH}), \]
\[ [\text{M} = \text{Co} (1) \text{ and Ni} (2)] \text{ and} \]
\[ [\text{Ni}^{\text{II}}_2\text{Dy}^{\text{III}}_2\text{L}_2(\text{CH}_3\text{CN})_2] 2(\text{CH}_3\text{CN}) \]
(3), have been characterized and, in particular 3, display for the first time 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.

Kieran Griffiths, Christopher W. D. Gallop, Alaa Abdul-Sada, Alfredo Vargas, Oscar Navarro and George E. Kostakis*

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