

Homogeneous Catalysis

Heteronuclear 3 d/Dy^{III} Coordination Clusters as Catalysts in a Domino Reaction

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

In memory of Prof. Yiannis Elemes

Abstract: Three isoskeletal tetranuclear coordination clusters with general formula $[M^{II}_{2}Dy^{III}_{2}L_{4}(EtOH)_{6}](CIO_{4})_{2}\cdot 2EtOH$, (M = Co, 1; M = Ni, 2) and $[Ni^{II}_{2}Dy^{III}_{2}L_{4}CI_{2}(CH_{3}CN)_{2}]\cdot 2CH_{3}CN$ (3), have been synthesized and characterized. These airstable compounds, and in particular 3, display efficient homogeneous catalytic behavior in 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^[1] was driven by their aesthetically pleasing structures,^[2-4] however the interest burgeoned due to the 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 coordination clusters. Apart from the employment of an heptanuclear Ce^{IV}Mn^{IV}₆ coordination cluster 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 its use in transformations involving unprotected amines.[11-16]

We recently initiated a project aimed at developing dual catalytic coordination clusters and to achieve this goal, compounds that retain their topology in solution are required. 3d/Dy^{III} coordination clusters possessing a defect dicubane topology derived from (*E*)-2-(2-hydroxy-3-methoxybenzylidene-amino)phenol (H₂L),^[17] pose as ideal candidates to serve this pur-

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pose. 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(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 the general formula $[M^{II}_{2}Dy^{III}_{2}L_{4}(EtOH)_{6}]$ -(ClO₄)₂·2 EtOH (M=Co, 1; M=Ni, 2) (Figure 1). Each 3d metal has an octahedral geometry and each



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

Dy^{III} center has a square-antiprismatic geometry. Two different coordination modes can be found for the organic ligand (see Scheme S1 in the Supporting Information), 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 m/z 1506.9719 and at m/z 736.0393 which perfectly correspond to two fragments, $[Co_{2}^{II}Dy_{2}^{III}L_{4}(CIO_{4})-H]^{+}$ and $[Co_{2}^{II}Dy_{2}^{III}L_{4}(MeOH)_{2}-H]^{2+}$, respectively (see Figures S1 and S2). Similarly, for 2, peaks at m/z 1520.0169 and m/z 744.55 correspond to {[Ni¹¹₂Dy¹¹¹₂L₄- ${[Ni_{2}^{II}Dy_{2}^{III}L_{4}(MeOH)-(EtOH)] +$ $(MeOH)_2(EtOH)] + 2H\}^+$ and $2H\}^{2+}$ fragments (see Figures S3 and S4), respectively. Therefore, in both cases, the ESI-MS data indicate that the dicationic $[M_{2}^{\parallel}Dy_{2}^{\parallel}L_{4}]^{2+}$ cores remain intact.



With the coordination clusters 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 one equivalent of water generated as a side 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.



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 (45,5R)-dimorpholinocyclopent-2-enone (Table 1, entry 1). This reaction was chosen to test the catalytic activity of coordination clusters 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 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 $Co(CIO_4)_2 \cdot 6H_2O$ nor Ni-(ClO₄)₂·6H₂O, the 3d metal precursors used in the synthesis of the coordination clusters, showed catalytic behavior (Table 1, entries 13 and 14).

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 coordination cluster, 2, was refluxed in acetonitrile for 1 h, affording an airstable, compound formulated as



 $[Ni^{II}_{2}Dy^{III}_{2}L_{4}Cl_{2}(CH_{3}CN)_{2}]$ ·2 CH₃CN (**3**) (Figure 2).^[21] A similar coordination behavior to **1** and **2** (see Scheme S1) is observed for the organic moieties in **3** but, interestingly, a perchlorate to chlorine transformation is observed.^[22] The Ni^{III} atoms have an octahedral geometry with one vertex occupied by a CH₃CN molecule, while Dy^{IIII} 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 *m/z* 1556.1150 and *m/z* 703.5109 correspond to { $[Ni^{III}_{2}Dy^{III}_{2}L_{4}Cl_{2}(CH_{3}CN)(CH_{3}OH)] + 4H$ }⁺ and { $[(Ni^{II}_{2}Dy^{III}_{2}L_{4}] - H$ }²⁺ fragments (Figures S5 and S6), respectively.



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

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2

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.

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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 5aor 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.

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 theory (DFT) at the B3LYP/6-311G** level employing the polarizable continuum media (PCM) formalism were carried out on model compounds **4 f**, **5 a**, **6**, and **7** (Figure 3). The overall energy profile together with the calculated NMR data (Table T1 in the Supporting Information) highly

suggests that a) the pathway from intermediate 6-5 a towards the final product is highly favorable-which thus confirms that the catalysis takes place prior to this step, b) intermediate 6-5 a 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.

In conclusion, we report herein the first examples of a series of custom-designed, catalytically active 3d/Dy^{III} coordination clusters. These are the first results towards the development


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



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

Chem. Eur. J. 2015, 21, 1-5

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3

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of dual catalytic coordination clusters. A careful choice of the organic ligand has allowed the synthesis of coordination clusters that remain intact in 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 spectroscopy of the diamagnetic $(Ni^{II}_2Y^{III}_2)$ analogue as well theoretical studies of the active catalytic species are underway. As the synthetic strategy to obtain 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

Compounds 1 and 2: Dy(OTf)₃ (61 mg, 0.1 mmol), $M(ClO_4)_2$ 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 one 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.

Compound 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 μ L, 0.5 mmol) were added in CH₃CN (20 mL), and the resulting mixture was refluxed for one 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 in the same yield by altering Ni(ClO₄)₂·6H₂O for NiCl₂ 6H₂O.

Crystallography

C₇₂**H**₉₂**Cl**₂**Co**₂**Dy**₂**N**₄**O**₂₈ (1): $M = 1975.25 \text{ gmol}^{-1}$, monoclinic, space group $P2_1/n$ (no. 14), a = 12.8246(4), b = 20.9395(5), c = 15.3815(5) Å, $\beta = 108.997(4)^\circ$, V = 3905.6(2) Å³, Z = 2, T = 173.0 K, $\mu(\text{Cu}_{\text{K}\alpha}) = 14.667 \text{ mm}^{-1}$, $\rho_{\text{calcd}} = 1.680 \text{ g cm}^{-3}$, 25962 reflections measured (7.4° $\leq 2\Theta \leq 142.898^\circ$), 7561 unique ($R_{\text{int}} = 0.0490$, $R_{\text{sigma}} = 0.0482$) which were used in all calculations. The final R_1 was 0.0378 ($l > 2\sigma(l)$) and wR_2 was 0.0981 (all data).

C₇₂**H**₉₂**C**₁₂**Dy**₂**N**₄**Ni**₂**O**₂₈ (2): $M = 1974.81 \text{ gmol}^{-1}$, monoclinic, space group P_{2_1}/n (no. 14), a = 12.7440(4), b = 20.9329(5), c = 15.3458(5) Å, $\beta = 108.920(4)^{\circ}$, V = 3872.6(2) Å³, Z = 2, T = 173 K, $\mu(\text{Mo}_{K\alpha}) = 2.539 \text{ mm}^{-1}$, $\rho_{calcd} = 1.694 \text{ g cm}^{-3}$, 19340 reflections measured (4.798° $\leq 2\Theta \leq 58.67^{\circ}$), 8980 unique ($R_{int} = 0.0330$, $R_{sigma} = 0.0510$) which were used in all calculations. The final R_1 was 0.0374 ($l > 2\sigma(l)$) and wR_2 was 0.0883 (all data).

C₆₄**H**₅₆**Cl**₂**Dy**₂**N**₈**Ni**₂**O**₁₂ (3): *M* = 1642.48 g mol⁻¹, triclinic, space group *P*1 (no. 2), *a* = 11.696(3), *b* = 11.973(4), *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(Mo_{Ka}) = 2.975 mm⁻¹, ρ_{calcd} = 1.669 g cm⁻³, 17540 reflections measured (4.768° ≤ 2*Θ* ≤ 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 ($l > 2\sigma(l)$) and wR_2 was 0.1584 (all data).

CCDC-1012311 (1), CCDC-1012312 (2), CCDC-1038641 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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4



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Custom-designed catalysts: Three airstable compounds formulated as $[M_2^{II}Dy_2^{III}L_4(EtOH)_6](CIO_4)_2 2EtOH,$ $[M = Co (1) and Ni (2)] and <math>[Ni_2^{III}Dy_2^{III}L_4CI_2(CH_3CN)_2] 2CH_3CN (3)$, have been characterized. Compound **3**, in particular, displays for the first time efficient homogeneous catalytic behavior in the room-temperature synthesis of *trans*-4,5-diaminocyclopent-2-enones from 2-furaldehyde and primary or secondary amines under a non-inert atmosphere.

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