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Efficient Ni^{II}_{2}Ln^{III}_{2} Electrocyclization Catalysts for the Synthesis of trans-4,5-Diaminocyclopent-2-enones from 2-Furaldehyde and Primary or Secondary Amines

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ABSTRACT: A series of heterometallic coordination clusters (CCs) [Ni^{II}_{2}Ln^{III}_{2}(L1)]Cl(CH\(_{2}\)CN)\(_{2}\) \(2\)CH\(_{2}\)CN [Ln = Y (1Y), Sm (1Sm), Eu (1Eu), Gd (1Gd), or Tb (1Tb)] were synthesized by the reaction of (E)-2-(2-hydroxy-3-methoxybenzylidene-aminophenol) (H\(_{2}\)L1) with NiCl\(_{2}\)(H\(_{2}\)O) and LnCl\(_{3}\)(H\(_{2}\)O) in the presence of Et\(_{3}\)N at room temperature. These air-stable CCs can be obtained in very high yields from commercially available materials and are efficient catalysts for the room-temperature domino ring-opening electrocyclization synthesis of trans-4,5-diaminocyclopent-2-enones from 2-furaldehyde and primary or secondary amines under a non-inert atmosphere. Structural modification of the catalyst to achieve immobilization or photosensitivity is possible without deterioration in catalytic activity.

INTRODUCTION

Polynuclear coordination clusters (CCs),\(^1,2\) assembled from organic ligands, transition-metal elements (3d), and/or lanthanide (4f) elements, are a burgeoning class of functional materials with fascinating structures.\(^3–8\) These materials are already used in areas ranging from molecular magnetism,\(^9–17\) biology,\(^18–20\) molecular imaging,\(^21\) magnetic resonance,\(^22\) and luminescence.\(^23–27\) However, one of the most common applications for coordination compounds, catalysis, is much less studied for polynuclear 3d/4f heterometallic CCs with classical N,O-donor ligands\(^28–34\) than for organometallic compounds.\(^35,36\) The difference in the growth rates between the two research fields may reflect the fact that organometallic compounds are mainly of low nuclearity, so it is easier to determine a possible mechanism for the catalytic procedure.

Electrocyclizations are one of the most valuable transformations for the construction of carbon–carbon bonds. The Nazarov cyclization exemplifies such an electrocyclization, providing access to important and useful cyclopentones, and Lewis acids catalyze this cyclization.\(^37–39\) The interest in bifunctionalized cyclopentones arises from the fact that they are versatile building blocks in the synthesis of natural products such as (+)-Nakadomarin A.\(^40\) Batey and Li used a variety of Lewis acids for the synthesis of trans-4,5-diaminocyclopentanones (Scheme 1) from the domino condensation/ring-opening/electrocyclization reaction of furaldehyde with amines.\(^41\) In this study, Dy(OTf)\(_{3}\) and Sc(OTf)\(_{3}\) were found to be the best catalysts, with 10% loadings. However, Sc(OTf)\(_{3}\) gave higher yields with primary amines (R\(^2\) = H; see Scheme 1) than Dy(OTf)\(_{3}\). This reaction proceeds in high yields with the use of acidic ionic liquids under solvent-free conditions\(^42\) or with the use of N-sulfonylimine, with p-toluenesulfonamide acting as a leaving group.\(^43\) However, in both cases, the reaction works only for secondary amines.

We have recently developed a new generation of 3d/4f CCs and have explored their catalytic behavior. The Schiff base H\(_{2}\)L1\(^44\) (Scheme S1 in the Supporting Information), along with 3d and 4f ions affords tetranuclear M\(^{II}\)Ln\(^{III}\)\(_{2}\) (M = Co or Ni) CCs possessing a defect dicubane topology with two divalent 3d ions (center) and two trivalent 4f ions (wings) (Scheme S1, middle).\(^35,45\) In this specific topology, five out of six, and six out of seven or eight, coordination sites are occupied by H\(_{2}\)L1 for the 3d and the Dy\(^{III}\) centers, respectively (Scheme S1, right). Recently, we reported that compound [Ni\(^{II}\)\(_{2}\)Dy\(^{III}\)\(_{2}\)(L1)\(_{4}\).]

Scheme 1. Schematic Representation of trans-4,5-Diaminocyclopentanones

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In our quest to develop these catalytic species further and to (a) seek lower cost materials and (b) investigate its possibility of immobilization, we decided to (i) extend our study to other lanthanides and (ii) to tune the organic periphery of the H$_2$L$_1$ ligand. Synthetic, catalytic, and theoretical issues are discussed in this report.

### EXPERIMENTAL SECTION

**Materials and methods.** 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 VNMR solution-state spectrometer at 500 MHz at 30 °C using residual isotopic solvent (DMSO, $\delta = 2.50$ ppm) as an internal reference. Chemical shifts are quoted in parts per million (ppm). Coupling constants (J) are recorded in units of Hz. IR spectra of the samples were recorded over the range of 4000–650 cm$^{-1}$ on a PerkinElmer Spectrum One FT-IR spectrometer fitted with an UATR polarization accessory. ESI-MS data were obtained on a VG Autospec Fissions instrument (El at 70 eV). TGA analysis was performed on a TA Instruments Q500 model (TA, Surrey, U.K.) under nitrogen and at a scan rate of 10 °C/min.

**Synthetic Procedures.** For the synthesis of ligands, see the Supporting Information (ESI).

#### Synthesis of 1Ln (Ln = Y, Sm, Eu, Tb, Dy).

**H$_2$L$_1$** (0.2 mmol, 48 mg), and Et,N (0.5 mmol, 69 μL) were added to a solution of MeCN (20 mL), and then washed with cold MeCN (20 mL) and Et$_2$O (0.1 mmol, 24 mg) and YCl$_3$·H$_2$O (0.1 mmol, 30 mg) were added and the resultant solution was heated under reflux for 2 h. The brown/yellow precipitate that settled as the mixture was allowed to cool was filtered and washed off with cold MeCN (20 mL) and Et$_2$O (10 mL). The precipitate was then collected and dried overnight at 60 °C. Yield: 74%, based on Y.

**1Sm-A** (0.1 mmol), and Et,N (0.5 mmol, 69 μL) were added and the mixture was stirred for 10 min. NiCl$_2$·6H$_2$O (0.1 mmol, 24 mg) and YCl$_3$·H$_2$O (0.1 mmol, 30 mg) were added and the resultant solution was heated under reflux for 2 h. The brown/red precipitate that settled as the mixture was allowed to cool was filtered and washed off with cold MeCN (20 mL) and Et$_2$O (10 mL). The precipitate was then collected and dried overnight at 60 °C. Yield: 90%, based on Y.

Crystals for single-crystal XRD were obtained by dissolving 3Y (25 mg) in DMF (10 mL). The solution was stirred for 10 min before filtration. The filtrate underwent vapor diffusion with Et$_2$O after 12 days clear green crystals suitable for XRD study were obtained. Elemental analysis for Ni$_3$Y$_2$(C$_5$H$_7$NO$_3$)$_6$Cl$_2$(CH$_2$CN)$_3$ (3Y): C 56.31, H 3.97, N 5.02; found: C 56.64, H 3.63, N 5.21.

**Compound 4Y.** To a solution of MeCN (20 mL), H$_2$L$_4$ (0.2 mmol), and Et,N (0.5 mmol, 69 μL) were added and the mixture was stirred for 10 min. NiCl$_2$·6H$_2$O (0.1 mmol, 24 mg) and YCl$_3$·H$_2$O (0.1 mmol, 30 mg) were added and the resultant solution was heated under reflux for 2 h. The brown/red precipitate that settled as the mixture was allowed to cool was filtered and washed off with cold MeCN (20 mL) and Et$_2$O (10 mL). The precipitate was then collected and dried overnight at 60 °C. Yield: 93%, based on Y. Crystals for single-crystal XRD were obtained by dissolving 4Y (25 mg) in DMF (10 mL). The solution was stirred for 10 min before filtration. The filtrate underwent vapor diffusion with Et$_2$O after 3 weeks, small green crystals suitable for XRD study were obtained. Elemental analysis for Ni$_3$Y$_2$(C$_5$H$_7$NO$_3$)$_6$Cl$_2$(CH$_2$CN)$_3$ (4Y): C 59.65, H 4.21, N 4.74; found: C 59.84, H 3.60, N 4.92.

**General Catalytic Protocol.** In air, powdered 4 Å molecular sieves (100 mg) were weighed into a 10 mL capped vials equipped with magnetic stirring bars. The use of molecular sieves is crucial for the reaction, since 1 equiv of water is generated as a side product. MeCN (dry, 4 mL), fufural (0.5 mmol, 41 μL), secondary amine (1 mmol), and the appropriate amount of catalyst (10%–15% total Dy) were added. The mixture was stirred at room temperature from 2 to 24 h, and the reaction was followed by thin layer chromatography (TLC). The reaction mixture was diluted with DCM (20 mL) and filtered through Celite. The resultant solution was concentrated under reduced pressure and the residue purified by column chromatography (20%–30% ethyl acetate in hexanes). The products were obtained as red or yellow oils, which solidified on standing.

**Crystallography.** Data for 2Y, 3Y, and 4Y (ω-scans) were obtained at the University of Sussex by use of an Agilent Xcalibur Eos Gemini Ultra diffractometer with CCD plate detector under a flow of nitrogen gas at 173(2) K using Mo Kα radiation ($\lambda = 0.71073$ Å).

**CrysAlis CCD and RED software programs** were used, respectively, for data collection and processing. Reflection intensities were corrected for absorption by the multiscan method. Data for 1Sm-A, 1Sm-B, 1Sm-C, and 1Eu-A were collected at the UK National Crystallography Service, University of Southampton on a Rigaku Saturn 724+ area detector mounted at the window of an FR-E+ rotating anode generator with a Mo anode ($\lambda = 0.71075$ Å) under a flow of nitrogen gas at 100(2) K. The X-ray data were collected and processed using Rigaku CrystalClear, except 1Eu-A, where Rigaku Oxford Diffraction CrystalsPro was used for data processing. Crystal structures 1Sm-B, 2Y, and 4Y were solved by dual-space method with SHELXT, whereas 1Sm-A, 1Sm-C, 1Eu-A, and 3Y were solved using charge flipping methods with Superflip. All crystal structures were then refined on $F^2$ by full-matrix least-squares refinements using SHELXL. 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, Olex2, and WINGX packages; graphics were prepared with Crystal Maker. Crystallographic details are given in Table S1 in the ESI (CCDC Nos. 1442674–1442680).

**Computational Details.** Energy minimization calculations on computationally designed model compounds (see Results and Discussion) were made within the Kohn–Sham density functional theory (DFT) approach at the B3LYP/SDD and B3LYP/6-311G* levels, with the Gaussian 09 software. The Jmol program was used for visualization purposes.

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RESULTS AND DISCUSSION

With the goal of developing effective molecular catalysts with low cost, we reasoned that replacement of DyIII with lanthanides of lower cost would allow us to evaluate the relationship between cost and effectiveness. Thus, we attempted to isolate and characterize the analogues of 1DY with Y (1Y), Sm (1Sm), Eu (1Eu), Gd (1Gd), and Tb (1Tb), following the similar reaction procedure that gave 1DY. The synthetic protocol specifies that, when the blend Dy(OTf)₃/[(NiClO₄)₂·6H₂O or NiCl₂·6H₂O/H₂L1/ Et₃N (molecular ratio of 1/1/2/5) in CH₃CN (20 mL) is refluxed for 1 h, the result, after filtration, is the formation of yellow-greenish crystals in moderate yield. Since the reactions to produce the 1Y, 1Sm, 1Eu, 1Gd, and 1Tb gave large amounts of filtrate, we decided to further characterize the constituent species. A range of techniques such as ESI-MS, elemental analysis, infrared (IR) spectroscopy, and TGA showed that these filtrates were similar to that from 1DY. IR spectra of 1Y, 1Sm, 1Eu, 1Gd, and 1Tb are similar to that of 1DY (see the ESI). The TGA data (Figures S12–S17 in the ESI) for all solid compounds indicated the loss of four CH₃CN molecules (lattice and coordinated) up to 290 °C and decomposition at higher temperatures. ESI-MS spectra of all species were similar, with two main peaks corresponding to the [Niᴵᴵ⁺Lnᴵᴵ⁺(L₁)₂Cl(CH₃CN)(CH₃OH)]⁺ and -[Niᴵᴵ⁺Lnᴵᴵ⁺(L₁)]²⁻ fragments (Figures S1–S7 in the ESI). Finally, elemental analyses are consistent with the calculated values without lattice CH₃CN molecules. IR, TGA, and ESI-MS analyses were performed three times from different batches, with similar results.

In our attempts to grow crystals, several unexpected products were structurally characterized, indicating that the synthesis of these species is not a simple task. For example, our effort to obtain crystals of 1Sm resulted in the synthetic characterization of three different compounds, formulated as [Niᴵᴵ⁺Smᴵᴵ⁺(CO₃)₂(C₆H₅)₂]-L1)₂(L')₃(OH)₂] (1Sm-A), [Niᴵᴵ⁺Smᴵᴵ⁺(L₁)₄(O-Van)] (1Sm-B), and [Smᴵᴵ⁺(OH)₃(L₁)₄(HL₁)]·2CH₃CN (1Sm-C), where L' is 2-aminophenol and O-Van is ortho-vanillin (see the ESI). In our attempt to obtain crystals of 1Eu, a compound formulated as [Niᴵᴵ⁺Euᴵᴵ⁺(L₁)₄(CO₃)Cl₂·(H₂O)₄] (1Eu-A) was obtained. The latter molecule is isoskeletal to compounds recently reported by Ke et al.

The next step was to characterize the catalytic activity of these species using the catalytic protocol developed in our previous study. In order to ascertain that the catalytic activity of these species is driven solely by the 4f ions, various blank tests were performed (see Table S1). First, three Ni⁺ salts with three different loadings (Table S1, entries 2–10) were used in the prototype reaction. NiCl₂ was found to catalyze the reaction with very high loadings and very low yields after 24 h (Table S2 in the ESI, entry 2) reflecting that its contribution is negligible for the shorter time period. An in situ mixture of Ni salt and ligand (Table S2, entries 11–13) gave none of the anticipated product after 24 h. In Baty’s protocol, since Dy(OTf)₃ was found to be an excellent catalyst using a loading of 10 mol %, our next step was to use other lanthanide salts (Table S1, entries 14–20) along with yttrium salts. YIII has a size and Lewis acidity similar to HoIII, and the use allows a catalytic reaction to be monitored with NMR (H, ¹³C, ¹⁵N, or ⁸⁹Y), because of its diamagnetic character. Astonishingly, Y(OTf)₃ showed similar excellent catalytic performance (Table S1, entry 14) to Dy(OTf)₃, and the lanthanide chlorides showed poorest performance (Table S1, entries 15–20). The next task was to utilize a mixture of Ni and Ln salts (Table S1, entries 21–26), which showed that the presence of the Ni salt had an almost negligible influence on the catalytic performance. Finally, the use of Ni(ClO₄)₂ and Dy(OTf)₃ or Y(OTf)₃ (Table S1, entries 27 and 28) showed an insignificant influence of the Ni source on the catalytic performance. The Y salt was better than the Dy salt. All these experiments demonstrated the superior catalytic behavior of 1DY (use of only 1 mol %; see Table 1, entry 1) over the simple metal salts as catalysts and the insignificant role of Ni⁺ in the catalysis. As shown in Table 1, 1Sm, 1Eu, 1Tb, and 1Gd (entries 2–5) catalyze the reaction in moderate to good yields in comparison to 1DY but show higher yields than simple salts. When 1Y (Table 1, entry 6) was involved, a catalytic performance similar to 1DY was observed. A further decrease of the catalytic amount of 1Y to 0.5% loading results in excellent conversion (Table 1, entry 7). The higher efficacy of YIII than LnIII in Lewis acid catalysis has been previously reported, but no rationale has been proposed. All attempts to recover the 1Ln catalyst, in order to reuse it, was unsuccessful.

Taking into account the cost of the metal salts, the yttrium derivative (1Y) was used in further experiments. Compound 1Y shows similar or better catalytic behavior than 1DY, along with various secondary or primary amines (see Table 2).

The excellent results that were obtained using even lower catalyst loadings (0.5% for 1Y, instead of 1.0% for 1DY), along with the less-expensive lanthanide source, led us to consider the possibility that 1Y could be structurally modified to achieve immobilization and demonstrate photosensitivity. We recently reported a library of 19 modified Schiff-base organic ligands that offer coordination environment similar to that in H₁L₁. Among these, the three organic ligands shown in Scheme 2 were selected for the synthesis of the corresponding tetranuclear CCs. Other considerations were (i) to increase the solubility, as well to offer the possibility for deposition of these species on surfaces by the introduction of an allyl group (H₂L₂); (ii) to create “photosensitive” catalysts by inclusion of a naphtho group (H₃L₃); and (iii) to combine both of these features (H₄L₄).
From ligand H₂L₂ (Scheme 2, left), in a slightly different synthetic ratio to 1Y, a compound formulated as [NiII₂Y₃(L₂)₂Cl₄(DMF)₂]₂Cl₂ (DMF)₂ (2Y) (Figure 1A) was obtained. Also, the ligands H₂L₃ and H₂L₄ (Scheme 2, center and right), with slightly different synthetic ratios, gave [NiII₂Y₃(L₃)₂Cl₄(DMF)₂]₂DMF 2Et₂O (3Y) and [NiII₂Y₃(L₄)₂Cl₄(DMF)₂]₂DMF (4Y) (Figure 1C), respectively. These compounds were characterized by X-ray crystallography (Figure 1), IR, ESI-MS, and TGA (see the ESI). Single-crystal studies indicate that compounds 2Y, 3Y, and 4Y are isoskeletal to 1Dy, while the ESI-MS data indicate that all three compounds retain their core structures in solution, shown by two main peaks corresponding to the [{NiII₂Y₃(L)₄Cl₄}]²⁻ and [{NiII₂Y₃(L)₄Cl₄}]²⁺ fragments. Each NiII center coordinates to six atoms (O₅N environment) possessing an octahedral geometry and each YIII center coordinates to seven atoms (O₅NCl environment) possessing a pentagonal bipyramidal geometry.

The catalytic activity of 2Y, 3Y, and 4Y toward the prototype reaction is shown in Table 2. Compounds 2Y and 4Y are not as efficient, relative to 1Y (1.0% loading, instead of 0.5% loading, Table 2. Comparison of Catalytic Activity of 1Y, 2Y, 3Y, and 4Y with Secondary and Primary Substrates, along with 1Dy, for Comparison

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aReaction conditions: 1 mmol amine, 0.5 mmol 2-furaldehyde, 100 mg of 4 Å MS, 4 mL of anhydrous MeCN catalyst, and room temperature.

bCatalyst loading calculated per equivalent of 1Ln. cAs determined by ¹H NMR spectroscopy.

Scheme 2. Three Modified Organic Ligands (H₂L₂, H₂L₃, and H₂L₄) Used for the Synthesis of 2Y, 3Y, and 4Y, Respectively

From ligand H₂L₂ (Scheme 2, left), in a slightly different synthetic ratio to 1Y, a compound formulated as [NiII₂Y₃(L₂)₂Cl₄(DMF)₂] (2Y) (Figure 1A) was obtained. Also, the ligands H₂L₃ and H₂L₄ (Scheme 2, center and right),
and slightly lower yields), but these results can be attributed to the presence of the sterically demanding naphtho groups. When 3Y was employed as a catalyst (Table 2), yields similar to those with 1Y were obtained. As we reported previously, the reaction occurs with primary amines, the corresponding deprotonated Stenhouse salts are formed (entries 6−9). The ring closing of the salt is promoted by the use of very dilute HCl, leading to the corresponding trans-4,5-diaminocyclopent-2-enones.

To explore further the possible immobilization of these catalysts, we attempted to synthesize the novel organic ligands H₄L5 and H₄L6 shown in Scheme 3 (see the ESI for synthesis details). Ligand H₄L5 offers a coordination environment similar to that in H₂L1; therefore, it was expected to form coordination polymers upon complexation with the Niᴵᴵ and Yᴵᴵᴵ salts. However, H₄L5 is only slightly soluble in polar solvents such as N,N’-DMF or DMSO. Organic ligand H₄L6 was synthesized, expecting a higher solubility, but similar to H₄L5, it is only slightly soluble in polar solvents. Our efforts to synthesize the corresponding coordination polymers have not yet been successful.

Computational studies showed that it was possible to modify ligand sterics without compromising the electrostatic properties that are key to the activities of the complexes. Renditions of the molecular electrostatic potential (MEP) for H₂L2, H₂L3, and H₂L4 are shown in Figure 2. The results also suggest that the charge distribution within the O−O−N−O core pattern directly interacting with the metals is a function of the conformation of the ligands.

Figure 1. X-ray crystal structures of 2Y (top), 3Y (middle), and 4Y (bottom). Color code: green = Niᴵᴵ; light blue = Yᴵᴵᴵ; yellow = C; red = O; pale blue = N; light green = Cl. Hydrogen atoms and disordered solvent molecules are omitted for the sake of clarity.

Scheme 3. Protonated Form of the Modified Organic Ligands H₄L5 (R = H) and H₄L6 (R = C(CH₃)₃)

Figure 2. Rendition of the molecular electrostatic potential (MEP) of H₂L2 (upper), H₂L3 (middle), and H₂L4 (lower) organic ligands: (left) bound and (right) free conformation.

CONCLUSIONS

The collective data on this simple and high yielding isoskeletal series of Niᴵᴵ,Lnᴵᴵᴵ CCs, supported by structurally homologous Schiff base ligands, shows remarkable catalytic activity in the formation of trans-4,5-diaminocyclopent-2-enones from 2-furaldehyde and primary or secondary amines. The Niᴵᴵ contribution is negligible and, therefore, it is safe to deduce that the domino reaction is driven solely by the 4f or Y ion. Remarkably, the employment of YᴵᴵΙ instead of Dyᴵᴵᴵ makes lower loading and lower-cost catalysts possible. We show that
the functionalization of the organic skeleton is feasible (2Y, 3Y, and 4Y), without impairing the catalytic activity. Moreover, our results suggest that the modified species 2Y and 4Y, which have allyl groups, can be immobilized by deposition on surfaces. Further work on this aspect is in progress. We are currently exploring the possibilities of utilizing 3d/4f or 3d/Y CCs as tandem catalysts in other organic transformations.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00720.

ESI-MS, TGA, and IR of 1Ln. ESI-MS, TGA and IR of 2Y−4Y; 1H NMR, and ESI-MS of H2L1, H2L2, H2L3, H2L4, and H2L5; 1H NMR of catalytic products from Table 2; Tables S1 and S2, Schemes S1 and S2, and Figures S1−S22 (PDF)

Crystallographic data (CIF)

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**Notes**

The authors declare no competing financial interest.

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