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Journal Name

ARTICLE

## Tetranuclear 3d/4f coordination clusters as highly efficient catalysts for Friedel Crafts alkylation

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A series of custom-designed high yield isoskeletal tetranuclear 3d/4f coordination clusters showing high efficiency as catalysts with low catalytic loadings in Friedel Crafts alkylation are described for the first time. The possibility to alter the 3d and the 4f centers in these catalysts without altering the core topology allows to further confirm their stability via EPR and NMR, as well to gain insights regarding the plausible reaction mechanism, showcasing their usefulness of these bimetallic systems as catalysts

Polynuclear Coordination Clusters (CCs), assembled by organic ligands, transition metal (3d) and/or lanthanide (4f) elements, represent a rapidly expanding class of materials.<sup>1–4</sup> However, only a few and recent examples showed the use of these materials as catalysts.<sup>5–8</sup> Friedel–Crafts (FC) reactions<sup>9</sup> consist one of the most important carbon – carbon bond forming reactions in organic and medicinal chemistry. In recent years, catalysts based on zinc or lanthanide elements have been extensively employed in FC reactions and sizeable development has taken place.<sup>10,11</sup> In particular, the indole ring system represents one of the most abundant and important heterocycles in nature exhibiting wide-ranging biological activity.<sup>12</sup> The nucleophilic addition of aldehydes or ketones to indoles, in the presence of a Lewis acid, is a facile route towards the synthesis of bisindolylmethane (BIMs) derivatives with only one equivalent of water generated as a side product. BIMs have recently been shown to be useful in the treatment of fibromyalgia<sup>13</sup>, antibacterial agents<sup>14</sup> and even in the prevention of cancer.<sup>14</sup> Various catalytic systems and metal salts have been reported for the synthesis of BIMs, however these methods suffer from a number of disadvantages such as expense; toxicity of reagents; high temperatures, high catalytic loading (stoichiometric–10%) and photosensitivity (silver salts).<sup>15–18</sup>

In 3d/4f chemistry, 4f centres may be replaced by Y<sup>III</sup> or Gd<sup>III</sup> without altering the core topology,<sup>19</sup> therefore permitting <sup>89</sup>Y NMR<sup>20</sup> or EPR<sup>21</sup> for characterization of the solution species, as well as allowing study of the catalytic reaction in situ to gain mechanistic insights. Also, the possibility to alter the 3d centres while retaining the topology<sup>22,23</sup> may provide more insights regarding the reaction mechanism, due to the different coordination behaviour to substrates (heteroatoms N, O or S),

anticipated to be seen when Co or Ni or Cu or Zn are used. We recently committed to studying the catalytic properties of tetranuclear 3d/4f CCs possessing a rigid defect dicubane topology assembled solely by the Schiff base organic ligand (*E*)-2-(2-hydroxy-3-methoxybenzylidene-amino)phenol (*H*<sub>2</sub>L) (Scheme S1). We showed that a series of isoskeletal<sup>24</sup> M<sup>II</sup><sub>2</sub>Ln<sup>III</sup><sub>2</sub> (M = Co or Ni, Ln = Y, Nd, Eu, Gd, Tb, Dy) CCs, effectively catalyse a domino reaction at room temperature.<sup>8,25</sup> These heterometallic species remain intact in organic solvents and this precise topology brings the 3d and the 4f centres very close (approximately 3.3 Å), allowing both metal centres to coordinate to the substrates and promote the coupling reaction in high yield, highlighting the catalytic utility of this tetranuclear bimetallic motif.

Being motivated from our previous results, and having in mind that Ln(OTf)<sub>3</sub><sup>26</sup> and Zn(ClO)<sub>4</sub>/Schiff base<sup>27</sup> compounds have been employed as catalysts in the reaction of indole derivatives with aldehydes and ketones with a loading of 10 mol%, we decided to synthesize and characterize a series of isoskeletal Zn<sup>II</sup><sub>2</sub>Ln<sup>III</sup><sub>2</sub> CCs and study, for the first time, their application towards FC reactions.

The combination under aerobic conditions of *H*<sub>2</sub>L with freshly prepared Ln(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in the presence of Et<sub>3</sub>N in EtOH afforded, in very good yields, precipitates subsequently crystallized by vapour diffusion of Et<sub>2</sub>O in *N,N'*-DMF solutions, affording the isoskeletal air-stable tetranuclear defect dicubane compounds with the general formula [Zn<sup>II</sup><sub>2</sub>Ln<sup>III</sup><sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DMF)<sub>2</sub>] where Ln is Y (**1Y**), Sm (**1Sm**), Eu (**1Eu**), Gd (**1Gd**), Dy (**1Dy**), Tb (**1Tb**) and Yb (**1Yb**) (Figure 1). These compounds were characterized in full by X-Ray crystallography (Tables S1–S2), IR, ESI-MS, TGA and elemental analysis (see ESI).

The Zn<sup>II</sup> ion adopts a slightly distorted octahedral geometry with an O<sub>5</sub>N donor set, while the Ln ion has a very distorted square antiprismatic geometry, by virtue of chelating nitrate anions, with an O<sub>7</sub>N donor set. Five out of six (Zn) and six out of eight (Ln) coordination sites are occupied by donors from the organic ligands. The remaining coordination sites are occupied by one DMF molecule (Zn) and one nitrate anion (Ln, chelated mode). For **1Y**, the Y...Zn

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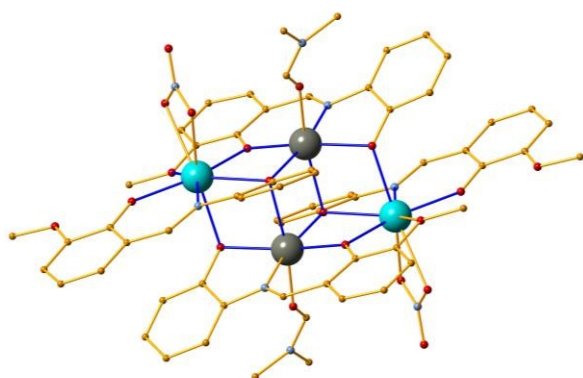
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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

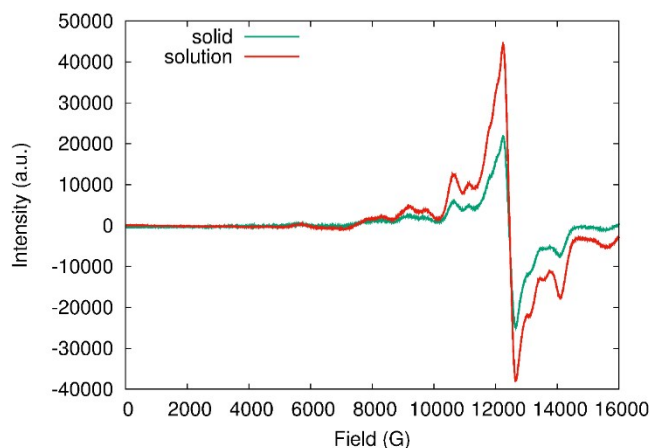
distances are 3.34882(7) and 3.5272(8) Å and the Zn...Zn distance is 3.2949 (8) Å; the other **1Ln** species are similar.



**Figure 1.** Molecular structure of **1Ln**. Colour code: Zn<sup>II</sup>: grey; Ln<sup>III</sup>: light blue; O: red; N: blue; C: yellow. Hydrogen atoms are omitted for clarity.

The identity of **1Ln** in solution was confirmed by electron spray ionization mass (ESI-MS) spectrometry studies; in all cases, we observed two peaks in the MS (positive-ion mode) at *m/z* which corresponds perfectly to the monocationic [Zn<sup>II</sup><sub>2</sub>Ln<sup>III</sup><sub>2</sub>L<sub>4</sub>(NO<sub>3</sub>)<sub>3</sub>]<sup>+</sup> and the dicationic [Zn<sup>II</sup><sub>2</sub>Ln<sup>III</sup><sub>2</sub>L<sub>4</sub>]<sup>2+</sup> fragments, respectively (see Figures S2-S19).

For further confirmation of the solution stability of **1Ln**, Q-band EPR studies of **1Gd** in both solid and solution (80% DMF, 20% Et<sub>2</sub>O) phase were performed, Figure 2. Simulations with PHI<sup>28</sup> confirm that the spectra owe to *S* = 7/2 Gd<sup>III</sup> ions with rhombic zero-field splitting (ZFS) (see Figure S1). The highly sensitive, finger-print-like ZFS of the *S* = 7/2 state directly indicates that the coordination environment of the Gd<sup>III</sup> ion is unchanged in solution.



**Figure 2.** Experimental EPR spectra at Q-band (34.0865 GHz) of **1Gd**, recorded at 7K in solid (green line) and solution phase (red line).

For benchmarking studies, indole and benzaldehyde were selected as reactants with **1Dy** as catalyst at 10% loading, and reaction parameters were subsequently optimized. The first set of reactions were performed in order to identify the ideal solvent system; after screening several solvents (Table S3), we identified that the ethanol/water (2/1) solvent system (Table S3, Entry 9) provided the best catalytic yield. The use of DMF, acetonitrile or EtOH as solvent (Table S3, Entries 4 – 6), resulted in the same product but in lower yields, indicating that the presence of H<sub>2</sub>O is crucial to obtain high yields. No conversion to product was observed in low polarity solvents in which **1Dy** is insoluble (Table S3, entries 1-3), suggesting

the catalytic action is homogeneous. We then performed a series of reactions using a 2.5% catalyst loading and varying the H<sub>2</sub>O/EtOH ratio (Table S4) and quantitative yields (entries 5-6) were obtained at 3/2 and 1/1 EtOH/H<sub>2</sub>O ratio. After selecting the optimum solvent system, we conducted reactions without **1Dy** catalyst (Table 1, Entry 1) and no product was obtained. Next, due to the heteronuclear (Zn/Ln) character of our molecules, Lanthanide and zinc triflates were utilized at 10 mol% loading (Table 1, entries 2-5), in order to identify their influence toward the bisindolylalkane product.

Yttrium triflate (Table 1, entry 3) was found to give quantitative yields and dysprosium triflate (Table 1, entry 2) produced only slightly lower yields, while zinc triflate (Table 1, entry 5) showed poor catalytic performance. Compound **1Dy** afforded almost quantitative yields of the desired product after 2h at 10 mol% loading. By use of **1Sm**, **1Eu**, **1Tb**, **1Gd**, **1Yb** comparable performance to **1Dy** was obtained, however the use of **1Y** at 2.5 mol% loading afforded the desired material in quantitative yield (Table 1, Entry 10). Promisingly, the catalyst loading for **1Y** could be decreased to 1 mol% with only a slight decrease in the yields (Table 1, entry 11), being far lower than other reported systems<sup>16,17,27</sup>. Importantly, reducing the catalyst loading for yttrium triflate to 2.5 mol% (Table 1, entry 4) resulted in a severe decrease in yield, compared to the ability of **1Dy** and **1Y** to maintain high yields at only a few mol%.

**Table 1.** Comparison of catalytic activity for Ln(OTf)<sub>3</sub> and (1-3)-Ln catalysts

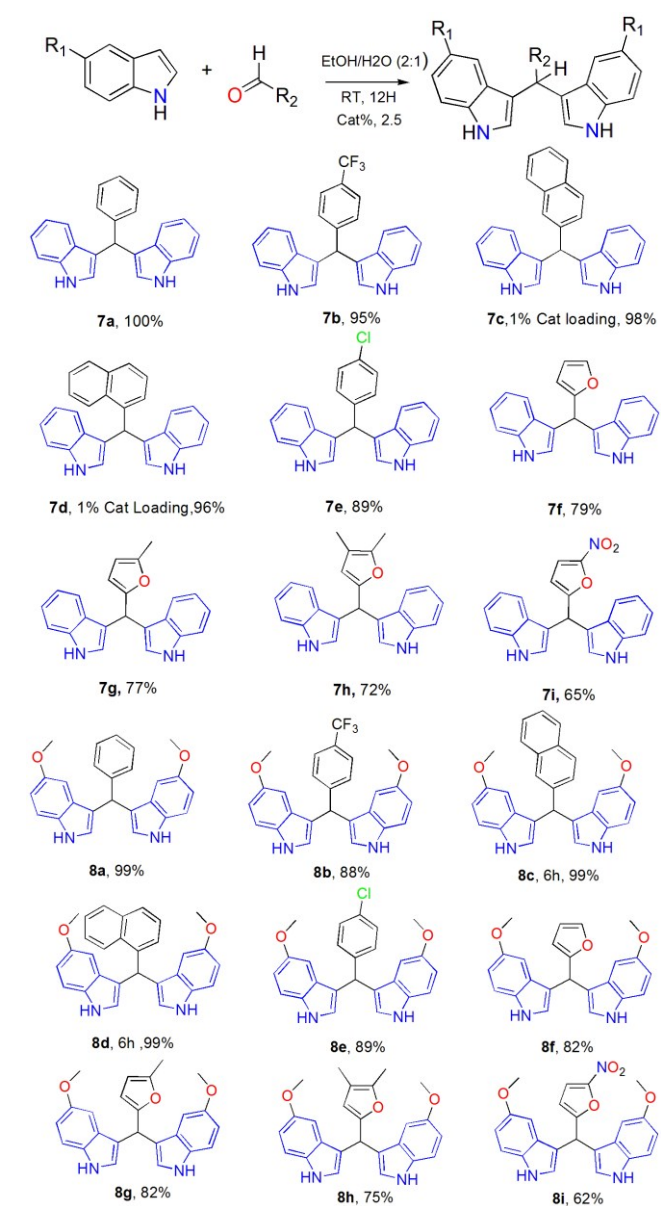
| Entry <sup>a</sup> | Catalyst             | Loading/mol% <sup>b</sup> | Time/ h | Yield/ % <sup>c</sup> |
|--------------------|----------------------|---------------------------|---------|-----------------------|
| 1                  | None                 | N/A                       | 12      | 0                     |
| 2                  | Dy(OTf) <sub>3</sub> | 10                        | 12      | 95                    |
| 3                  | Y(OTf) <sub>3</sub>  | 10                        | 12      | Quantitative          |
| 4                  | Y(OTf) <sub>3</sub>  | 2.5                       | 12      | 55                    |
| 5                  | Zn(OTf) <sub>3</sub> | 10                        | 12      | 18                    |
| 6                  | <b>1Dy</b>           | 10                        | 2       | Quantitative          |
| 7                  | <b>1Dy</b>           | 5                         | 2       | 96                    |
| 8                  | <b>1Dy</b>           | 2.5                       | 12      | 92                    |
| 9                  | <b>1Dy</b>           | 1                         | 12      | 87                    |
| 10                 | <b>1Y</b>            | 2.5                       | 12      | Quantitative          |
| 11                 | <b>1Y</b>            | 1                         | 12      | 96                    |
| 12                 | <b>1Sm</b>           | 2.5                       | 12      | 87                    |
| 13                 | <b>1Eu</b>           | 2.5                       | 12      | 53                    |
| 14                 | <b>1Tb</b>           | 2.5                       | 12      | 80                    |
| 15                 | <b>1Gd</b>           | 2.5                       | 12      | 75                    |
| 16                 | <b>1Yb</b>           | 2.5                       | 12      | 94                    |

<sup>a</sup> Reaction conditions: Indole, 1 mmol; benzaldehyde, 0.5 mmol; catalyst, 10mL EtOH/H<sub>2</sub>O (2:1); room temperature. <sup>b</sup> Catalyst loading calculated per equivalent of Ln<sup>III</sup>. <sup>c</sup> Determined by <sup>1</sup>H NMR spectroscopy.

We then explored the scope of the reaction by employing a variety of aldehydes and substituted indoles (Table 2). The reaction proceeds smoothly with very good to excellent yields. Products **7a**, **8c** and **8f** were characterized via single crystal X-Ray diffraction (Figure S20). The next step was to involve ketones in place of

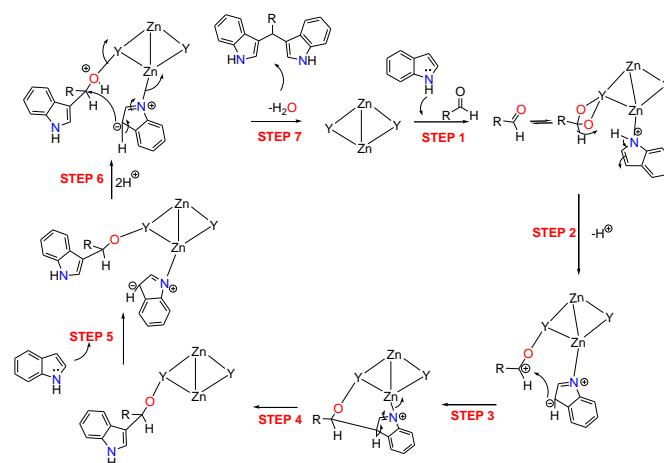
aldehydes. Long reaction times, even with a slight increase of the temperature (50 °C) did not yield any product with both aliphatic (acetone, cyclohexanone) and aromatic ketones (acetophenone) and no unexpected side products were observed. This opposite behaviour recalls the selective reduction of ketones in presence of aldehydes (Luche reaction).<sup>29</sup> In this reaction, aldehydes bond to Ln centres via hemiketal form, whilst ketone remains unprotected, thus reduced by NaBH<sub>4</sub>. Efforts to monitor the formation of the hemiketal form by NMR were not successful. To gain information regarding the reaction mechanism we performed UV-Vis binding studies of 2-naphthaldehyde with Zn(OTf)<sub>2</sub>, Dy(OTf)<sub>3</sub> and **1Dy** (Figure S21). **1Dy** is found to have almost double the rate of 2-naphthaldehyde quenching compared to Dy(OTf)<sub>3</sub>, and Zn(OTf)<sub>2</sub> is significantly slower than both. This observation indicates that 2-naphthaldehyde prefers coordination to Dy over Zn.

**Table 2.** **1Y** catalysed FC alkylation of indole and aldehydes.



a Reaction conditions; aldehyde, 0.5 mmol; substituted indole, 1 mmol; EtOH/H<sub>2</sub>O, (2:1) 10mL; room temperature; 12h. 2.5% Loading of **1Y**.

To gain further information regarding the plausible mechanism and to identify the limitations of the present catalysts, we decided to perform the following set of reactions. First, we employed an aliphatic aldehyde (cyclohexanecarbaldehyde) instead of an aromatic aldehyde in reaction with indole, that gave very low yields of the expected product **9** (Scheme S1) after 72 hours. Second, we examined substituted indoles such as 2-methyl-indole, 2-(trifluoromethyl)-indole, 3-methyl indole, indole-3-acetic acid and N-methyl indole in reaction with benzaldehyde. The use of 2-methyl-indole gave the expected product **10** (Scheme S1) in quantitative yield in only 2 hours, indicating that substitution in position 2 promotes the reaction. Compound **10** was characterized via single crystal X-Ray diffraction (Figure S22). However, the use of the electron withdrawing group -CF<sub>3</sub> in place of -CH<sub>3</sub> [reaction with 2-(trifluoromethyl)-indole] only gave a yield of 16%, product **11** indicating a substantial influence on the catalytic activity. The use of indole-3-acetic acid did not yield any product. A logical explanation for deterioration of catalytic activity is that indole-3-acetic acid is in competition with the benzaldehyde to coordinate to the Ln centre, leading to a poisoning of the catalyst, however the use of 3-methyl-indole did not result in the formation of the BIM. The latter indicates that if the most active site (C-3) of the indole group is blocked the reaction does not proceed. Finally, the reaction of N-methyl-indole with benzaldehyde did not yield in any product, showcasing that coordination of the nitrogen atom to Zn(II) is crucial.



**Scheme 1.** A plausible mechanism for the FC alkylation.

Despite the diamagnetic nature of **1Y**, characterizing it in the solution state by NMR proved difficult due to its asymmetry, dynamic behaviour, and its relatively low solubility. However, the peak areas for the imine, aromatic, and methoxy protons were all consistent with the structure as determined by X-ray crystallography, Figure 1. Gradually warming to 75 °C in 10 °C steps caused gradual broadening of the peaks, which then recoalesced on cooling back to room temperature, without any apparent decomposition of the complex. Using multiple solvent suppression, it was possible to monitor the smooth conversion of benzaldehyde and indole to the product in protonated 2:1 EtOH/H<sub>2</sub>O. With Y(OTf)<sub>3</sub>, the concentration of intermediates appeared to be very low, but with prolonged acquisition it was possible to identify a minor species using <sup>15</sup>N-HMBC. Its chemical shift of 113 ppm is distinctly different from indole (130 ppm) and the product (125 ppm), but the proton chemical shifts of 7.33 (127.9 ppm in <sup>13</sup>C-HSQC) and 4.99 ppm (too close to the



solvent peak to identify  $^{13}\text{C}$ -correlations) suggest that it may be the benzaldehyde-indole hemiaminal. In the absence of catalyst, the product forms very slowly (ca. 10% in 1 month), but under the same spectroscopic conditions it was not possible to detect the same correlations. This raises the prospect that it may well be a key intermediate, but more favourable conditions may be required to unambiguously identify it.

Given knowledge of the structure of the catalyst and the data given above, we propose the following mechanism for the FC reaction (Scheme 1). The first step of the reaction involves the coordination of the  $\text{N}_{\text{indole}}$  atom to the  $\text{Zn}^{\text{II}}$  and the  $\text{O}_{\text{carbonyl}}$  atom of the aldehyde to the Ln part of the catalyst (Step 1). In the presence of  $\text{H}_2\text{O}$  the aldehyde may coordinate to the Ln centre via its hydrated form. Then, deprotonation of the coordinated indole leads to the formation of negative centre at C-3 of the indole moiety (Step 2). The two organic moieties are very close [ $\text{Y}\cdots\text{Zn}$  distances are 3.34882(7) and 3.5272(8) Å] to favour the formation of benzaldehyde-indole hemiaminal, as suggested by the NMR studies, (Steps 3-4) followed by alkylation of one more indole moiety (Step 5). Finally, the catalytic cycle ends by a proton exchange with an additional indole moiety (Step 6) and release of the bis-adduct product and water and reform the active catalyst species (Step 7).

## Conclusions

Overall, the results presented herein confirm for the first time, that these tetranuclear CCs may indeed be useful as FC catalysts, with low catalyst loading. Our philosophy to alter the 3d or the 4f elements in these solution-stable bimetallic 3d/4f species allow us to confirm their stability via EPR and gain useful insights regarding the plausible reaction mechanism via NMR. Moreover, the possibility to tune the organic periphery of these catalysts,<sup>8,25</sup> achieving immobilization, showcases that the present catalysts are highly desirable and the appropriate vehicle to open new avenues in the fields of 3d/4f chemistry and catalysis. Further work is necessary to expand the scope of the present Zn/Ln CCs to other FC alkylation reactions, and this will be the focus of our future activities.

## Acknowledgements

We thank the EPSRC (UK) for funding (grant number EP/M023834/1), the University of Sussex for offering a PhD position to K.G., the EPSRC UK National Crystallography Service at the University of Southampton<sup>30</sup> for the collection of the crystallographic data for compounds **7a**, **8c**, **8f** and **10**, and the EPSRC UK National Electron Paramagnetic Resonance Service at The University of Manchester.

## Notes and references

‡**Catalytic Protocol.** To a mixed solution of  $\text{EtOH}/\text{H}_2\text{O}$  (2:1 in 10mL), aldehyde (0.5mmol) and Indole (1mmol) were added followed by catalyst (2.5% with respect to aldehyde). The resultant solution was stirred for 12H, upon which time product had precipitated. The cloudy solution was filtered and precipitate washed with hexanes (3x10mL) and water (3x10mL). For products which did not precipitate, the clear solution was concentrated under reduced pressure and extracted in ethyl acetate (30mL) from water (20mL). The ethyl acetate layer was dried with  $\text{MgSO}_4$  and concentrated under reduced pressure. The resulting oil was washed with Hexanes (60mL) resulting in a powdered solid which was further washed with water (3x10mL). Full Experimental Details are given in the Supporting Information. § CCDC 1452416-1452423

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