Controlling the Formation of Metallosupramolecular Assemblies by Metal Ionic Radii.

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Electronic Supporting Information

Spectroscopic and Analytical Measurements. $^1$H spectra were recorded at 25 °C on a Bruker Avance 500 MHz spectrometer. Chemical shifts are given in ppm with respect to CHD$_2$NO$_2$ or CHCl$_3$. Diffusion experiments were carried out at 400 MHz–Larmor frequency. Solutions (CD$_3$NO$_2$, 298 K, $[\text{complex}]_{\text{tot}} = 1\cdot10^{-3}$ M) of the complex were prepared in situ and left to equilibrate for 24 hrs. The pulse sequence used was the Bruker pulse program *ledbpgp2s* which employs stimulated echo, bipolar gradients and longitudinal eddy current delay as the z filter. The four 2 ms gradient pulses have sine-bell shapes and amplitudes ranging linearly from 2.5 to 50 G·cm$^{-1}$ in 16 steps. The diffusion delay was in the range 100-200 ms depending on the analyte diffusion coefficient, and the no. of scans was 32. The processing was done using a line broadening of 5 Hz and the diffusion coefficients were calculated with the Bruker processing package. Electrospray mass spectra (ESI-MS) were recorded from 10$^{-3}$ M solutions on a Bruker MicrOTOF-q instrument.

Synthesis of L$^1$.

To a round bottomed flask charged with 2,2’-bipyridine-6-thioamine (0.10 g, 0.46 mmol) and 1,3-di(α-bromoacetyl)benzene (0.067 g, 0.21 mmol) was added EtOH (50
ml) and the reaction refluxed for 8 hrs, after which time a white precipitated formed. Filtration followed by washing with EtOH (2 x 10 ml) and Et₂O (2 x 10 ml) gave the ligand L¹ as a white solid (0.075 g, 65 %). ¹H NMR (500MHz, CDCl₃) δ 8.68 (d, 2H, J = 4.3, H¹¹), 8.63 (s, 1H, H¹), 8.61 (d, 2H, J = 7.8, H⁵), 8.46 (d, 2H, J = 7.6, H⁷), 8.38 (d, 2H, J = 7.6, H²), 8.02 (d, 2H, J = 7.7, H³), 7.98 (t, 2H, J = 7.8, H⁶), 7.89 (t, 2H, J = 7.7, H⁹), 7.76 (t, 1H, J = 6.5, H²), 7.36 (t, 2H, J = 6.7 Hz, H¹⁰).

![1H/1H COSY (CD₃NO₂) of [Cd₂(L¹)₂]⁺ showing couplings between protons on the phenylene ring (red), the internal pyridine ring (blue) and the terminal pyridine ring (green).](image)

**Fig. 1** ¹H/¹H COSY (CD₃NO₂) of [Cd₂(L¹)₂]⁺ showing couplings between protons on the phenylene ring (red), the internal pyridine ring (blue) and the terminal pyridine ring (green).
Fig. 2 $^1$H/$^1$H COSY (CD$_3$NO$_2$) of [Zn$_5$(L$_1$)$_5$]$^{10+}$ showing couplings between protons on the phenylene ring (red), the internal pyridine ring (blue) and the terminal pyridine ring (green). The signal at 8.55 ppm corresponds to two overlapping proton signals from the internal and terminal pyridine rings.
Fig. 3 $^1$H/$^1$H NOESY (CD$_3$NO$_2$) of [Cd$_2$(L$^1$)$_2$]$^{4+}$ showing selected intra- (red) and inter-ligand (blue) through-space interactions.
Fig. 4 $^1$H/$^1$H NOESY (CD$_3$NO$_2$) of [Zn$_3$(L$^1$)$_3$$]^{10+}$ showing selected intra- (red) and inter-ligand (blue) through-space interactions.
Fig. 5 ESI-MS of \([\text{Zn}_5(L^1)_5](\text{ClO}_4)_{10}\) showing singly charged ions corresponding to \([\{\text{Zn}_2(L^1)\}(\text{ClO}_4)_3]^+\), \([\{\text{Zn}(L^1)_2\}(\text{ClO}_4)_3]^+\), \([\{\text{Zn}_2(L^1)_2\}(\text{ClO}_4)_3]^+\) and \([\{\text{Zn}_3(L^1)_3\}(\text{ClO}_4)_5]^+\) and a doubly charged ion corresponding to \([\{\text{Zn}_5(L^1)_5\}(\text{ClO}_4)_8]^{2+}\)

Table 1

Selected proton pairs in \([\text{Zn}_5(L^1)_5]^{10+}\) for which through-space couplings are observed and their shortest corresponding non-bonded distances taken from the solid-state structure (analogous values for \([\text{Cd}_2(L^1)_2]^{4+}\) are given in parentheses for comparison).

<table>
<thead>
<tr>
<th>proton pair</th>
<th>H⋯H dist. (Å)</th>
<th>comment</th>
</tr>
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<tbody>
<tr>
<td>(H^6\cdots H^2)</td>
<td>3.74 (5.20)</td>
<td></td>
</tr>
<tr>
<td>(H^7\cdots H^2)</td>
<td>3.32 (4.23)</td>
<td></td>
</tr>
<tr>
<td>(H^{11}\cdots H^3)</td>
<td>3.95 (5.37)</td>
<td></td>
</tr>
<tr>
<td>(H^5\cdots H^2)</td>
<td>4.09 (6.11)</td>
<td></td>
</tr>
<tr>
<td>(H^6\cdots H^3)</td>
<td>3.93 (4.46)</td>
<td></td>
</tr>
<tr>
<td>(H^6\cdots H^8)</td>
<td>3.82 (5.19)</td>
<td></td>
</tr>
<tr>
<td>(H^5\cdots H^3)</td>
<td>3.67 (4.72)</td>
<td></td>
</tr>
<tr>
<td>(H^5\cdots H^4)</td>
<td>4.64 (3.19)</td>
<td>only obs. in ([\text{Cd}_2(L^1)_2]^{4+})</td>
</tr>
</tbody>
</table>
Intra-strand

\[
\begin{align*}
H^4 \cdots H^1 & \quad 2.52 \ (4.32) \\
H^7 \cdots H^8 & \quad 2.23 \ (2.21) \quad \text{also obs. in } [\text{Cd}_2(L^1)_2]^4^+
\end{align*}
\]

References