Supplementary material for

Factors influencing mononuclear versus multinuclear coordination in a series of potentially hexadentate acyclic N₆ ligands: the roles of flexibility and chelate ring size.

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Figure S1: X-ray structure of the [Co(bmbu)]³⁺ cation.

The above structure showed extensive disorder in both the cation and perchlorate anions. The disorder was resolved to a certain extent but, despite this, an acceptable R1 value could not be obtained (R1 = 11.45 %). All atoms were refined isotropically as attempts to refine the structure anisotropically gave numerous atoms which exhibited non-positive-definite temperature factors. In the [Co(bmbu)]³⁺ cation, the entire bmbu ligand was found to be disordered over two sites, with approximately 54:46 occupancy. The conformation of the 7-membered chelate ring was found to be the same in both, attesting to a significant amount of rigidity and consistent with the ¹H NMR data for the complex (see main paper). The above diagram shows one of the two disordered components of the [Co(bmbu)]³⁺ cation.
**Mass spectra of complexes.**

All spectra were recorded in MeCN in the presence of formate as calibrant. The peak in each spectrum at highest m/z generally corresponds to \([\text{MLClO}_4]^+\) while that at lowest m/z generally corresponds to \([\text{ML}]^{2+}\). The presence of dimeric and trimeric species is indicated by the complex isotope pattern about the high m/z peak as discussed in the paper.

![Mass spectrum of \([\text{Mn(bmet)}](\text{ClO}_4)_2\)](image)

**Figure S2: Mass spectrum of \([\text{Mn(bmet)}](\text{ClO}_4)_2\)**
Figure S3: Mass spectrum of [Ni(bmet)](ClO$_4$)$_2$
Figure S4: Mass spectrum of [Zn(bmpp)](ClO₄)₂
Figure S5: Mass spectrum of $[\text{Co(bmpp)}][(\text{ClO}_4)_3]$
Figure S6: Mass spectrum of a 1:1 MeCN solution of [Ni(H₂O)₆](ClO₄)₂ and bmpt
Figure S7: Mass spectrum of a 1:1 MeCN solution of [Mn(H₂O)₆](ClO₄)₂ and bmot
Figure S8: Mass spectrum of a 1:1 MeCN solution of [Ni(H₂O)₆](ClO₄)₂ and bmot