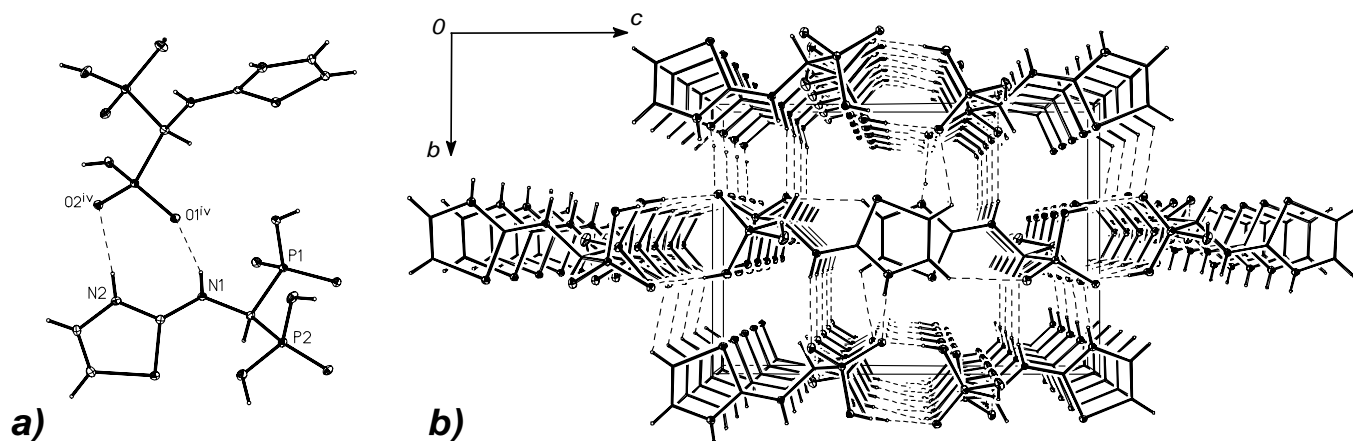


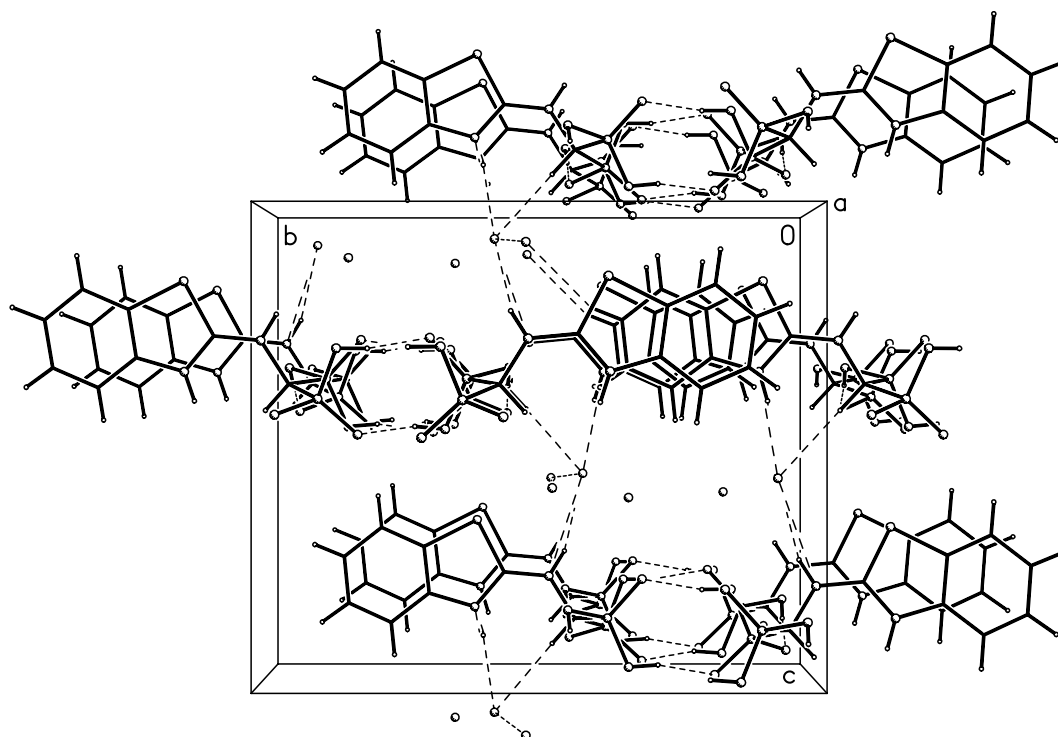
**Figure S1.**

R2,2(8) ring motif formed *via* the N1–H1N···O1<sup>iv</sup> and N2–H2N···O2<sup>iv</sup> bonds between the adjacent ribbons in **5** (a) and the crystal packing mode in the structure of the crystal (viewed down the *a* axis) (b). Dashed lines show hydrogen bonds.

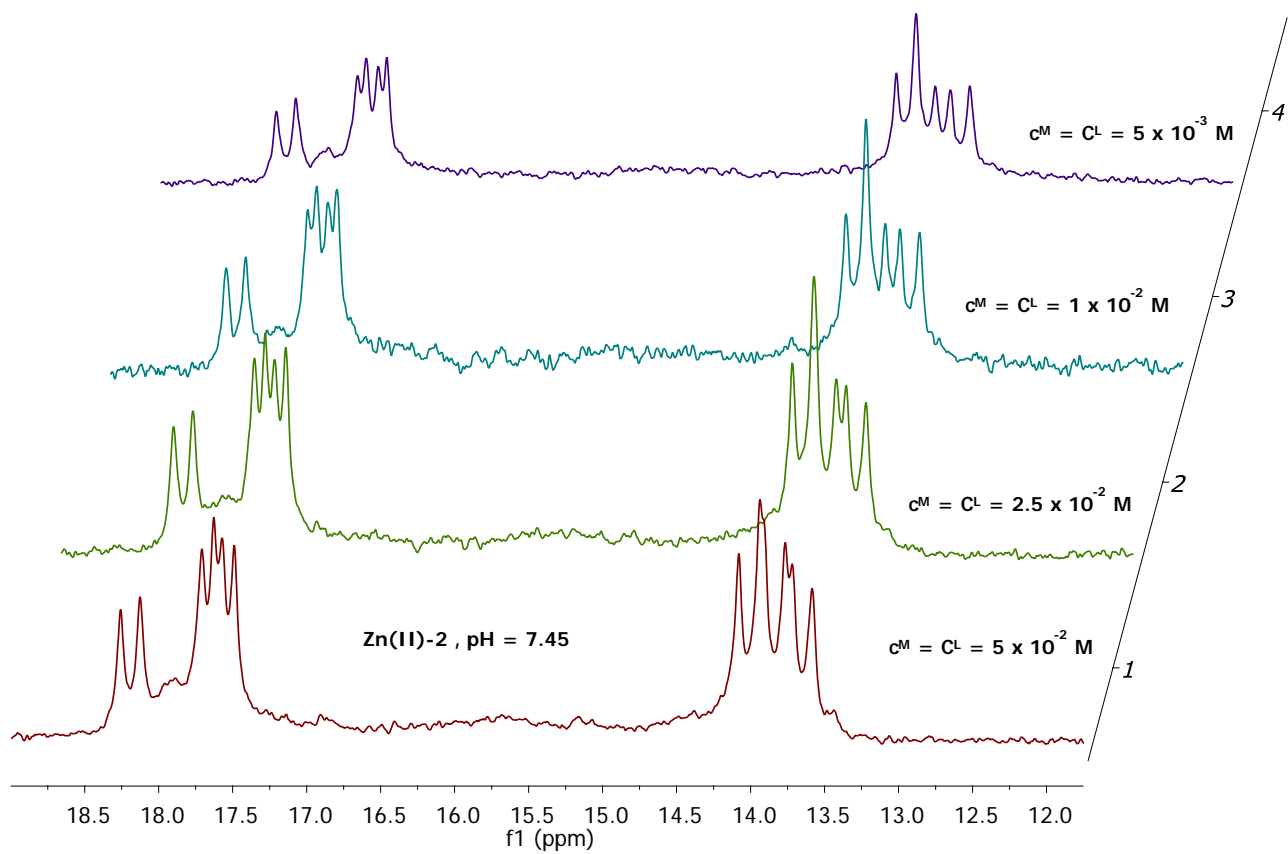


**Figure S2.**

The crystal packing mode in the structure of **6** (viewed down the *a* axis). Only O1W and O2W water molecules are shown. O1W-bonded hydrogen atoms are omitted.



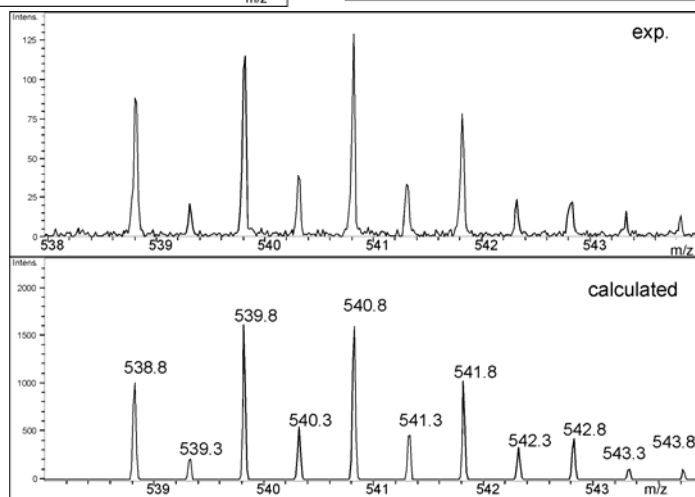
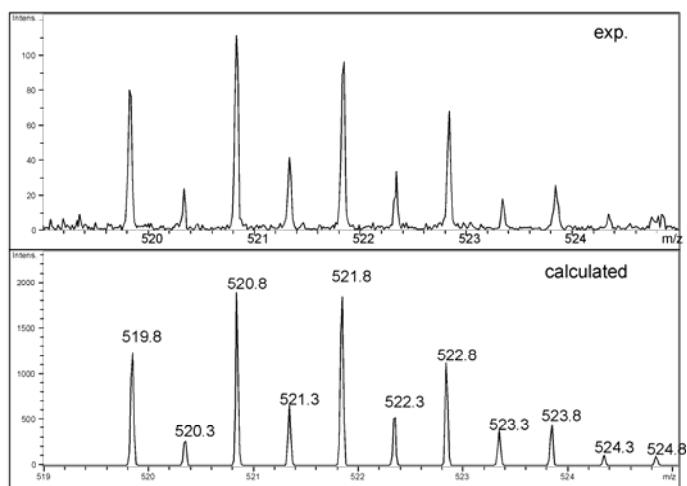
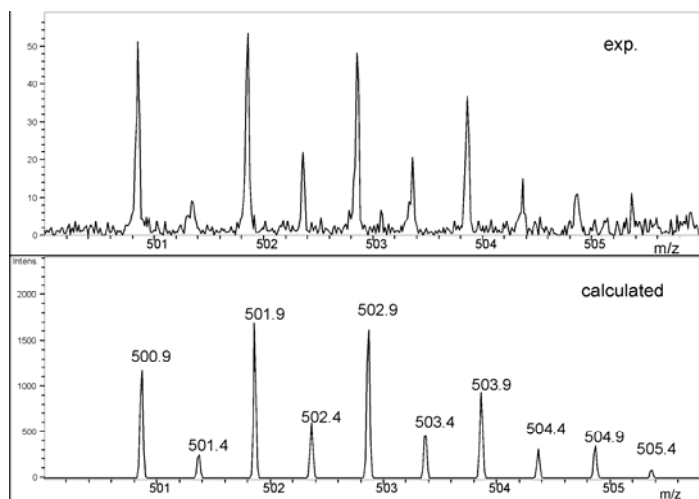
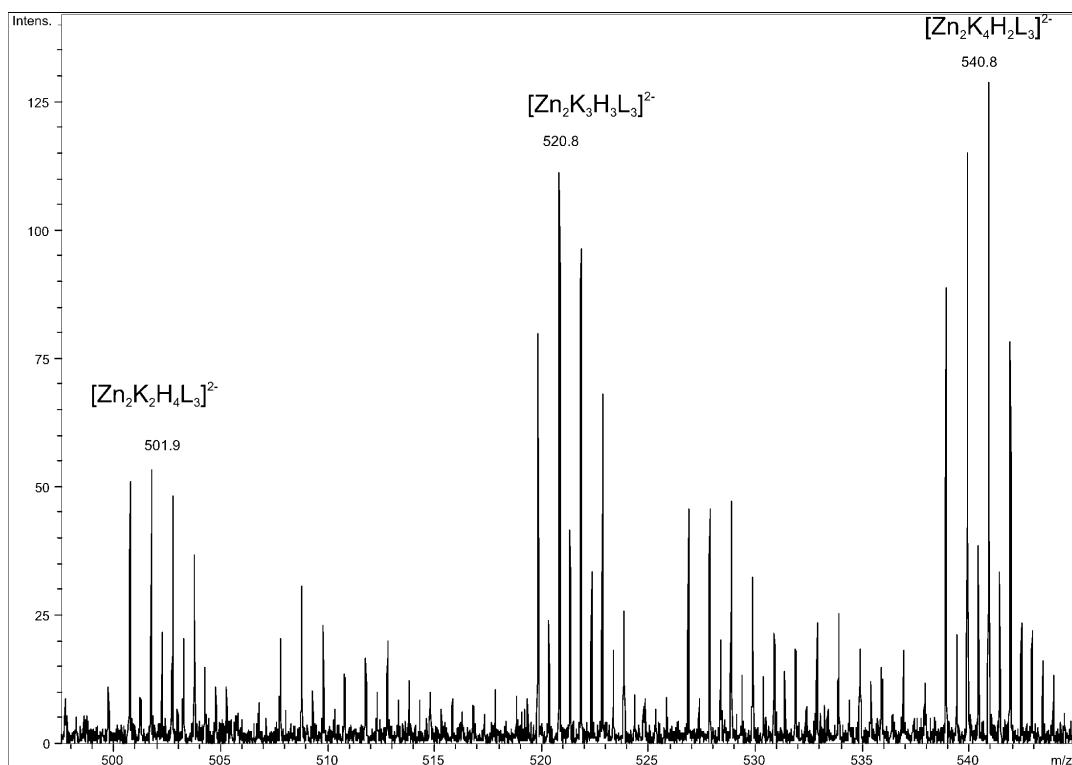
Effect of dilution on the  $^{31}\text{P}$  NMR spectra of the Zn(II)-2 system at pH = 7.45.



**Figure S4.**

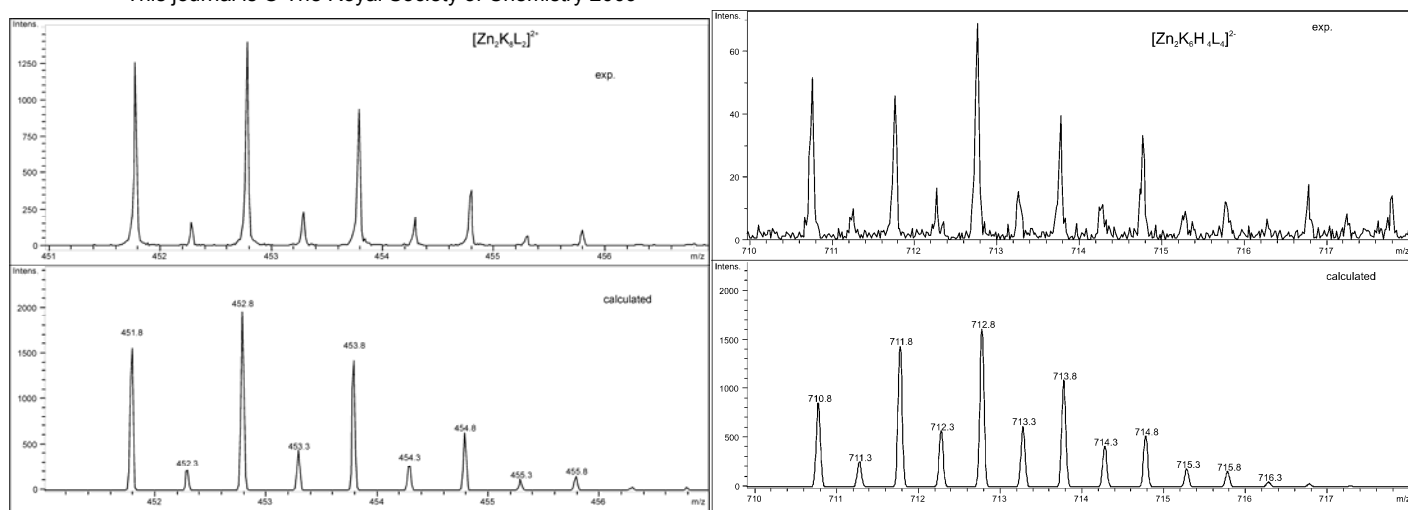
Supplementary Material (ESI) for Dalton Transactions  
ESI MS spectra confirming the stoichiometry of Zn(II) complexes with the studied ligands:

(a) Fragment of the experimental ESI-MS spectrum (negative ion mode) corresponding to the  $[\text{Zn}_2\text{K}_2\text{H}_4\text{L}_3]^{2-}$ ,  $[\text{Zn}_2\text{K}_3\text{H}_3\text{L}_3]^{2-}$ ,  $[\text{Zn}_2\text{K}_4\text{H}_2\text{L}_3]^{2-}$  species of Zn(II) with **1** and comparison of the experimental and calculated isotope distribution patterns for the representative 2:3 metal-to-ligand molar ratio species.

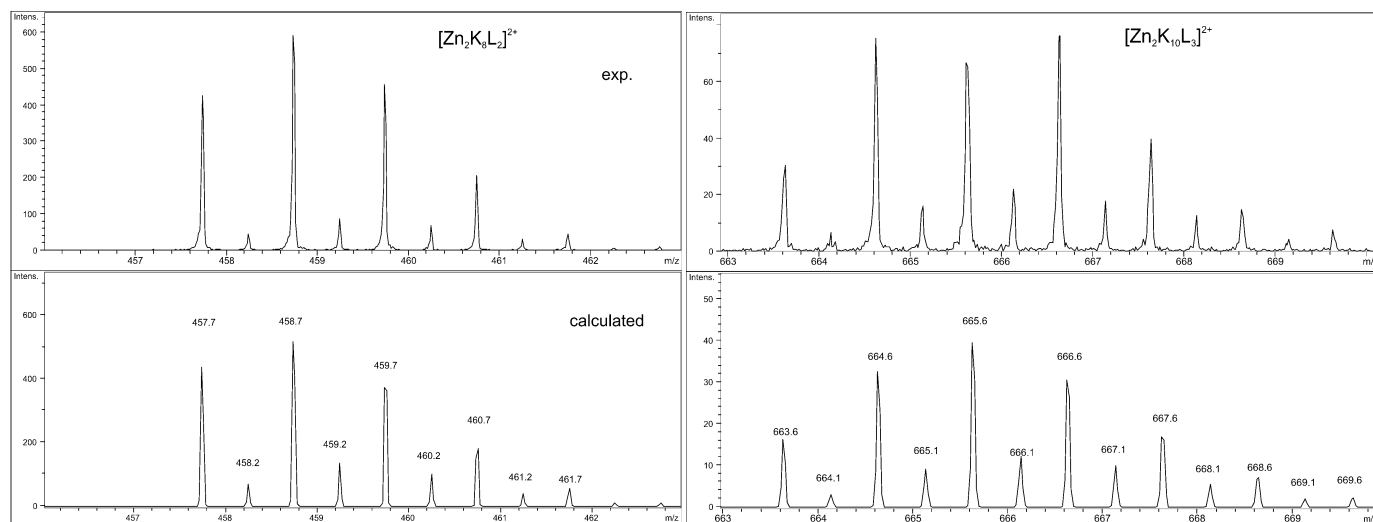


(b) 1:2 and 2:4 metal-to-ligand molar ratio species of Zn(II) with **1** (positive ion mode).

Supplementary Material (ESI) for Dalton Transactions  
This journal is © The Royal Society of Chemistry 2009

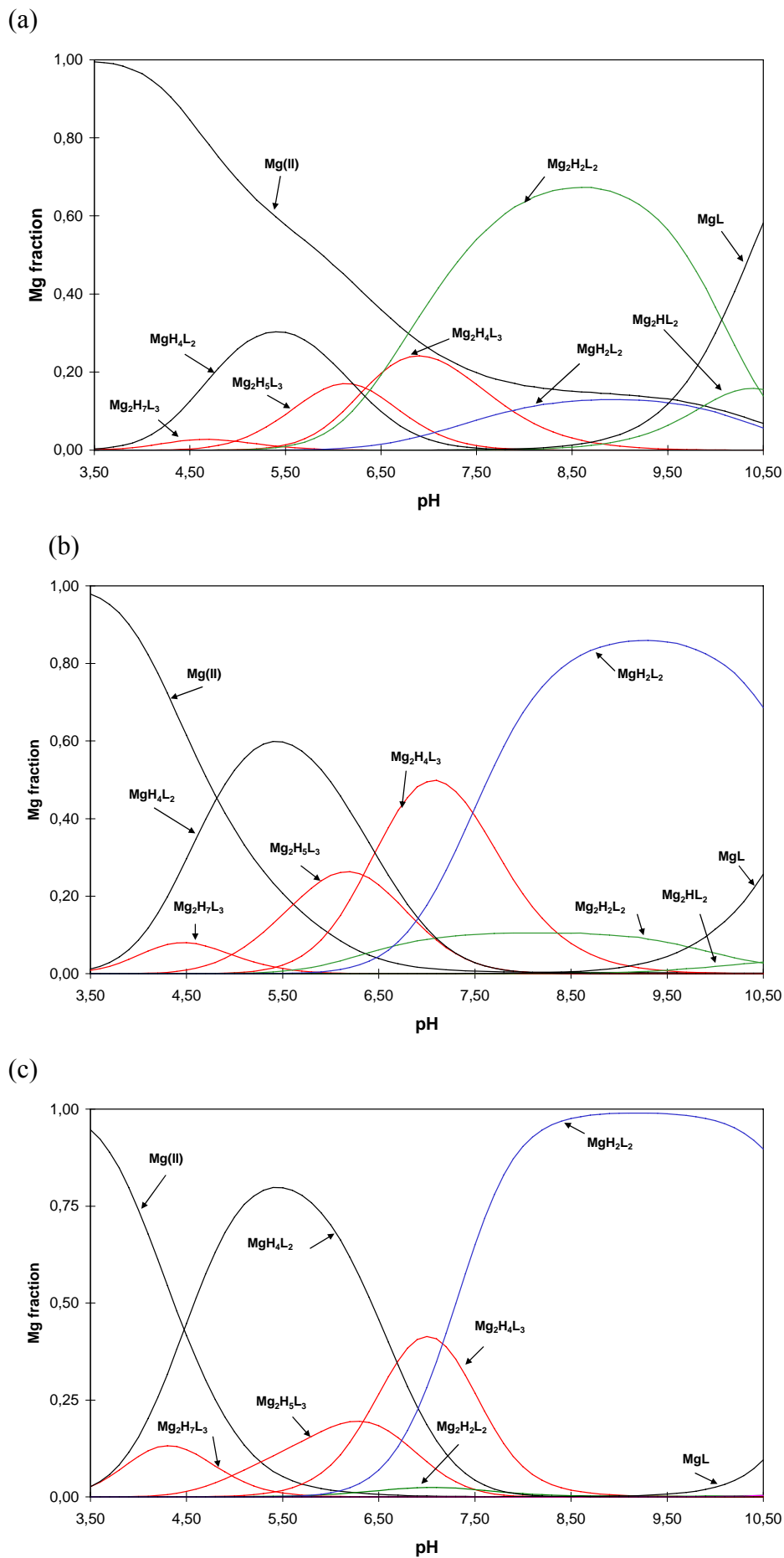


(c) Experimental and calculated isotope distribution patterns for the representative 1:2 (left) and 2:3 (right) metal-to-ligand molar ratio species of Zn(II) with **5**.



**Figure S5**

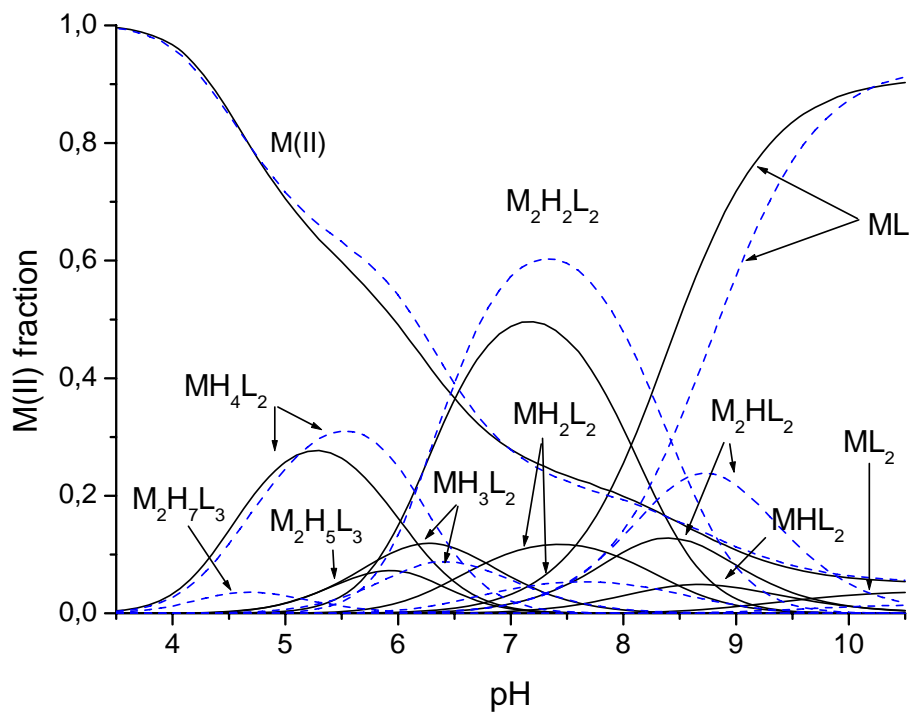
Supplementary Material (ESI) for Dalton Transactions

Representative species distribution diagrams for the Mg(II) systems with **2** at constant  $c_M = 1 \times 10^{-3}$  M and different ligand concentrations: (a)  $c_L = 1 \times 10^{-3}$  M, (b)  $c_L = 2 \times 10^{-3}$  M, (c)  $c_L = 3 \times 10^{-3}$  M.

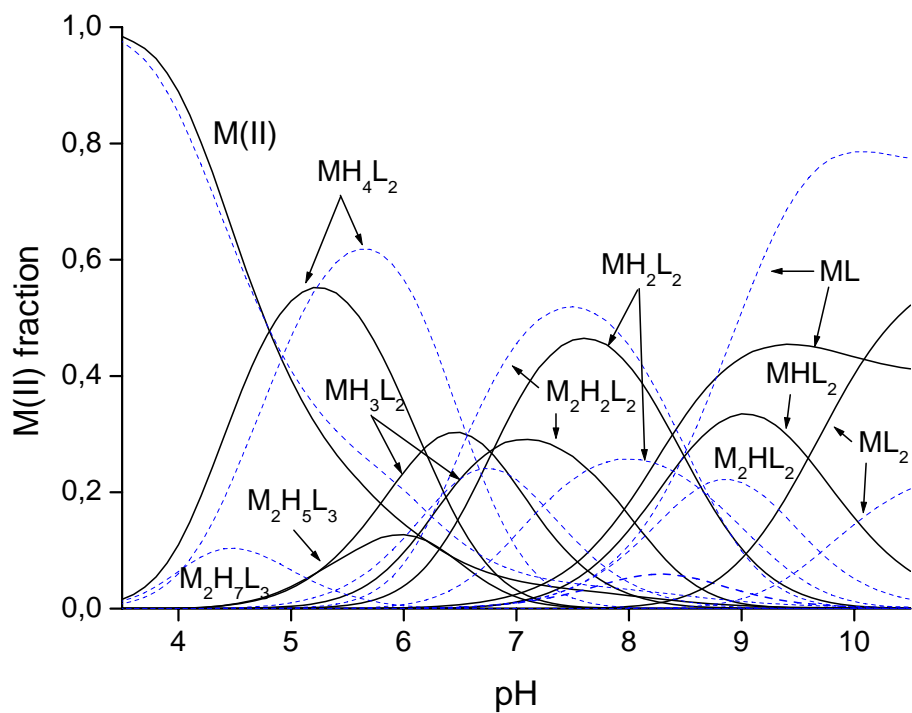
**Figure S6** Supplementary Material (ESI) for Dalton Transactions

Species distribution diagrams for the 1:1 (a) and 1:2 (b) Mg(II) (solid line) and Ca(II) (dashed line) systems with 5,  $c_M = 1 \times 10^{-3}$  M.

(a)

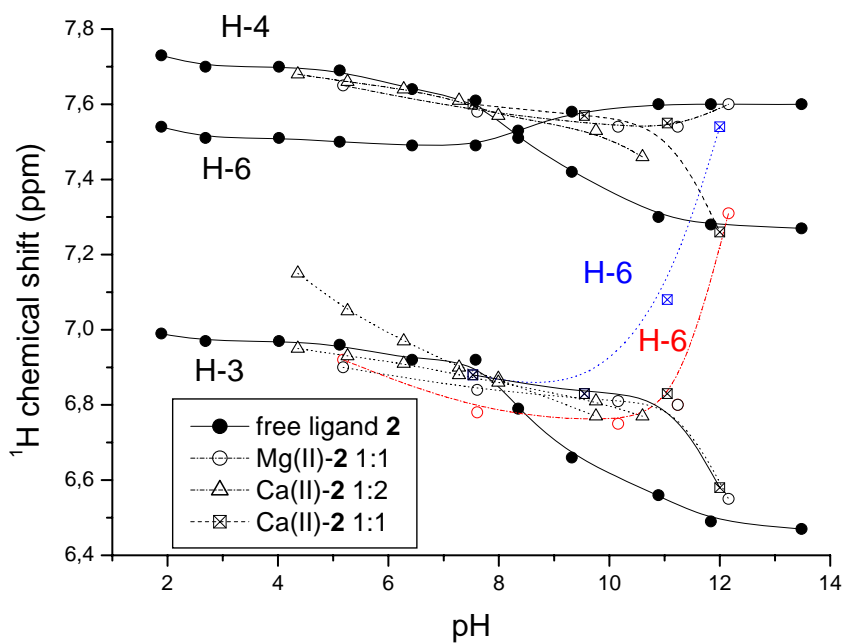


(b)



**Figure S7**

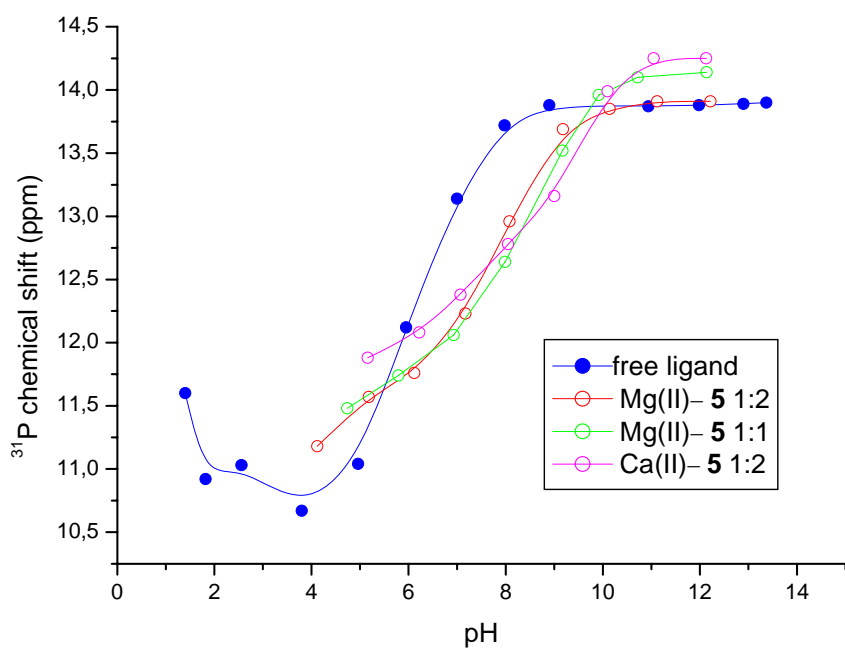
Supplementary Material (ESI) for Dalton Transactions  
Chemical Science, 2019, 10, 123456789  
Chemical shifts of the partially protonated H(6), H(4) and H(5) versus pH in the  $^1\text{H}$  NMR spectra performed for the Mg(II)-2 1:1 molar ratio system and for the Ca(II)-2 1:1 and 1:2 molar ratio systems.



**Figure S8.**

Supplementary Material (ESI) for Dalton Transactions

31P NMR titration curves for the Mg(II)-5 1:1 molar ratio system and for the Mg(II)-5 and Ca(II)-5 1:2 molar ratio systems.





**Table S1** Supplementary Material (ESI) for Dalton Transactions  
 Major peaks identified in the ESI-MS spectrum of the 1:2 and 1:1 molar ratio systems of Zn(II) with **1**, **2**, **4** and **5** and the corresponding species found by potentiometry

Zn(II)L system	Peaks $m/z^a$	Stoichiometries		Corresponding species found by potentiometry	
		positive mode	negative mode		
ligand <b>1</b>	397.8	$[\text{ZnK}_4\text{Na}_2\text{H}_2\text{L}_2]^{2+}$		$[\text{ZnH}_3\text{L}_2]^{3-}$ $[\text{ZnH}_2\text{L}_2]^{4-}$	
	451.8	$[\text{ZnK}_8\text{L}_2]^{2+}$		$[\text{ZnHL}_2]^{5-}$	
	500.9		$[\text{Zn}_2\text{K}_2\text{H}_4\text{L}_3]^{2-}$		
	519.9		$[\text{Zn}_2\text{K}_3\text{H}_3\text{L}_3]^{2-}$		
	538.9		$[\text{Zn}_2\text{K}_4\text{H}_2\text{L}_3]^{2-}$		
	557.9		$[\text{Zn}_2\text{K}_5\text{HL}_3]^{2-}$	$[\text{Zn}_2\text{H}_8\text{L}_3]$	
	597.8	$[\text{Zn}_2\text{K}_7\text{H}_3\text{L}_3]^{2+}$		$[\text{Zn}_2\text{H}_6\text{L}_3]^{2-}$	
	616.7	$[\text{Zn}_2\text{K}_8\text{H}_2\text{L}_3]^{2+}$		$[\text{Zn}_2\text{H}_5\text{L}_3]^3$	
	635.7	$[\text{Zn}_2\text{K}_9\text{HL}_3]^{2+}$			
	654.7	$[\text{Zn}_2\text{K}_{10}\text{L}_3]^{2+}$			
	667.3	$[\text{Zn}_2\text{K}_3\text{NaH}_{10}\text{L}_4]^{2+}$		$[\text{Zn}_2\text{H}_8\text{L}_4]^{4-}$ ,	
	691.8		$[\text{Zn}_2\text{K}_5\text{H}_5\text{L}_4]^{2-}$	$[\text{Zn}_2\text{H}_6\text{L}_4]^{6-}$	
	710.8		$[\text{Zn}_2\text{K}_6\text{H}_4\text{L}_4]^{2-}$	$[\text{Zn}_2\text{H}_5\text{L}_4]^{7-}$	
	ligand <b>2</b>	446.8	$[\text{ZnK}_7\text{HL}_2]^{2+}$		$[\text{ZnHL}_2]^{5-}$
465.8		$[\text{ZnK}_8\text{L}_2]^{2+}$		$[\text{ZnH}_2\text{L}_2]^{4-}$	
606.8		$[\text{Zn}_2\text{K}_2\text{Na}_2\text{H}_6\text{L}_3]^{2+}$		$[\text{Zn}_2\text{H}_8\text{L}_3]$	
618.8		$[\text{Zn}_2\text{K}_7\text{H}_3\text{L}_3]^{2+}$		$[\text{Zn}_2\text{H}_6\text{L}_3]^{2-}$	
637.8		$[\text{Zn}_2\text{K}_8\text{H}_2\text{L}_3]^{2+}$		$[\text{Zn}_2\text{H}_5\text{L}_3]^{3-}$	
656.8		$[\text{Zn}_2\text{K}_9\text{HL}_3]^{2+}$			
676.2		$[\text{Zn}_2\text{K}_{10}\text{HL}_3]^{2+}$			
738.8		$[\text{Zn}_2\text{K}_3\text{Na}_5\text{H}_6\text{L}_4]^{2+}$		$[\text{Zn}_2\text{H}_8\text{L}_4]^{4-}$	
758.8		$[\text{Zn}_2\text{K}_4\text{Na}_5\text{H}_7\text{L}_4]^{2+}$			
778.8		$[\text{Zn}_2\text{K}_8\text{H}_6\text{L}_4]^{2+}$			
ligand <b>4</b>		413.8		$[\text{ZnK}_2\text{H}_2\text{L}_2]^{2-}$	
	432.8		$[\text{ZnK}_3\text{HL}_2]^{2-}$		
	451.8		$[\text{ZnK}_4\text{L}_2]^{2-}$		
	529.7	$[\text{ZnK}_8\text{L}_2]^{2+}$			
	655.7		$[\text{Zn}_2\text{K}_4\text{H}_2\text{L}_3]^{2-}$		
	674.7		$[\text{Zn}_2\text{K}_5\text{HL}_3]^{2-}$		
	693.6		$[\text{Zn}_2\text{K}_6\text{L}_3]^{2-}$		
	733.6	$[\text{Zn}_2\text{K}_8\text{H}_2\text{L}_3]^{2+}$			
	752.6	$[\text{Zn}_2\text{K}_9\text{HL}_3]^{2+}$			
	771.6	$[\text{Zn}_2\text{K}_{10}\text{L}_3]^{2+}$			
	852.6	$[\text{Zn}_2\text{K}_4\text{Na}_2\text{H}_8\text{L}_4]^{2+}$			
	860.6	$\text{Zn}_2\text{K}_5\text{NaH}_8\text{L}_4]^{2+}$			
	ligand <b>5</b>	450.7	$[\text{Zn}_2\text{K}_6\text{L}_2]^{2+}$		$[\text{Zn}_2\text{H}_4\text{L}_2]$ $[\text{Zn}_2\text{H}_3\text{L}_2]^-$ $[\text{Zn}_2\text{H}_2\text{L}_2]^{2-}$ $[\text{Zn}_2\text{HL}_2]^{3-}$
		457.7	$[\text{ZnK}_8\text{L}_2]^{2+}$		$[\text{ZnH}_2\text{L}_2]^{4-}$ $[\text{ZnHL}_2]^{5-}$ $[\text{ZnL}_2]^{6-}$
625.7		$[\text{Zn}_2\text{K}_8\text{H}_2\text{L}_3]^{2+}$		$[\text{Zn}_2\text{H}_5\text{L}_3]^{3-}$	
644.7		$[\text{Zn}_2\text{K}_9\text{HL}_3]^{2+}$			
663.6		$[\text{Zn}_2\text{K}_{10}\text{L}_3]^{2+}$			